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MESOSCOPIC ADHESION OF POLY(DIMETHYLSILOXANE)

— Self-adhesion, Effects of Fillers, Surface Modification and Thin Top Layers

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de Rector Magnificus, prof.dr.ir. C.J. van Duijn, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op donderdag 10 mei 2007 om 16.00 uur

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Chapter 1

Introduction

1.1. Polymer coatings

Polymer coatings are used almost everywhere in our daily life for the purpose of decoration and/or protection of surfaces against various influences of, for instance, moisture, UV-radiation, chemical attack and mechanical damage [1]. In order to achieve long-term stability and durability under such conditions, good adhesion between polymer coatings and substrates is of great importance. With a growing number of applications of a broad range of polymer coatings in the industrial and consumer field, there is an increasing interest in understanding better the adhesion properties between polymer coatings and substrates.

1.2. Adhesion between solids

1.2.1. Adhesion

Adhesion has been studied intensively over the past 40 years. The problem of determining the adhesion between solid bodies in contact is important for understanding friction, wear, lubrication, adhesives, the agglomeration and dispersion of powders and colloidal particles, and many other phenomena [2]. As a complex, multifaceted phenomenon, adhesion involves factors such as surface chemistry, thermodynamics, polymer chemistry and physics, hydrodynamics, and mechanics [3].

Mittal [4] dealt with the term adhesion by dividing it into three categories: (i) basic or fundamental adhesion, (ii) thermodynamic or reversible adhesion, and (iii) experimental or practical adhesion. Basic or fundamental adhesion is defined as the summation of all interfacial intermolecular interactions, such as ionic, covalent, metallic, hydrogen bonding and van der Waals forces, between the contacting materials. This definition of adhesion is not helpful as it is almost not possible either to calculate the magnitude or to measure such adhesion forces in practical systems. Thermodynamic or reversible adhesion signifies the change in Gibbs (or Helmholtz) free energy per unit area when an interface is formed (or separated). The practical adhesion signifies the force or the work required to remove or detach a solid from another.

The measured practical adhesion value is strongly influenced by many factors, such as the surface chemistry, mechanical properties and surface roughness of the coating and substrate, the thickness of the coating, mode of failure, etc. This value can also be significantly different when different adhesion measurement techniques, parameters
of technique and measuring conditions are used [4].

1.2.2. Adhesion measurement techniques

In the field of science of adhesion, the search for a reliable and quantitative test of adhesion is of long-standing interest. Up to now more than 300 techniques have been developed for adhesion measurement of two solids in contact, such as a coating / substrate system. Packham [5] classified these methods as destructive and non-destructive methods. A comparison between some common destructive and non-destructive methods is given in a recent review [6]. In destructive methods, such as tensile, peel and shear experiments, the specimens typically undergo macroscopic irreversible deformation. Hence, bulk properties strongly influence the measured amount of adhesion. Moreover, difficulties are met when a broad range of materials are compared, because the measured values also depend on the test technique and test parameters.

The so-called non-destructive measurements are primarily used for the determination of the thermodynamic work of adhesion [6]. The two most common methods are the wetting method and the surface forces measurement method. The wetting method utilizes contact angle measurements of a range of liquids to estimate, indirectly, the surface energy and work of adhesion via different theories, such as the geometric mean approach [7] and harmonic mean approach [8]. Although several questionable simplifications are incorporated in the theories of contact angle measurements, this approach gives values of surface energy and work of adhesion that can be usefully applied in the context of the theory of adhesion [9-10]. This technique probes the surface of a solid material on the macroscopic scale using a liquid, and does not cause any deformation. Therefore measurements are generally not influenced by bulk properties, unless swelling or dissolution occurs. A disadvantage is that no direct information can be obtained from the contact between two solids.

A different approach to obtain values of work of adhesion involves the use of sensitive measurements of either the detachment force or the applied force combined with the radius of the contact zone, by using the surface force measurements [10]. The first surface forces apparatus (SFA) was developed by Tabor, Winterton and Israelachvili. These authors used this method for a direct determination of van der Waals’ forces between two smooth sheets of mica [11-12]. Nowadays the most popular SFA described in the literature are the atomic force microscope (AFM) and the so-called Johnson-Kendall-Roberts (JKR) apparatus. The AFM measures the force required to separate the two solids in contact (pull-off force) based on the force-displacement data. AFM gives information on the nanometer scale; therefore surface heterogeneity of the specimen may strongly influence the results. Moreover, care must be given when modifying the AFM tips in order to introduce functional groups for measurements.
With a JKR apparatus the external force \( P \) and the corresponding contact radius \( a \) are generally measured and the work of adhesion is obtained from these data following the proposal described in the classical paper of Johnson et al. on surface energy and the contact of elastic solids [13]. Pioneered by the work of Chaudhury et al. [14-15], this technique has been widely used, via contact mechanics [16], to study the adhesion between two solids when at least one solid is soft. In a standard JKR experiment, the contact deformation is in the mesoscopic scale. Therefore this method is less sensitive to very local surface heterogeneities and of great interest and importance in practical cases.

1.2.3. The JKR technique

In this thesis, the JKR technique is used as the main technique for studying the adhesion between two solids. The essential basis of the JKR theory is straight-forward. For a purely elastic contact between two spheres, the total energy of these two spheres is the sum of the work of adhesion, the stored elastic energy caused by their deformation and the potential energy of the applied load. The strain energy release rate, \( G \), is given by [13]

\[
G = \left( \frac{Ka^3}{R} - P \right)^2 \frac{2}{6\pi Ka^3}
\]  

(1.1)

where

\[
\frac{1}{K} = \frac{3}{4} \left[ \frac{1-v_1^2}{E_1} + \frac{1-v_2^2}{E_2} \right]
\]  

(1.2)

\[
\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}
\]  

(1.3)

\( P \) is an external force; \( K \) is the elastic constant. \( R_1 \) and \( R_2 \) are the radii of curvature of the two spheres. \( v_1, v_2 \) and \( E_1, E_2 \) are the Poisson ratios and elastic moduli of the two spheres, respectively.

For a purely elastic equilibrated system, \( G \) is equal to the thermodynamic work of adhesion, \( W \). Using this Griffith’s criterion, equation 1.1 can be written in the familiar JKR form as follows:

\[
a^3 = \frac{R}{K} \left[ P + 3\pi WR + \sqrt{6\pi WR P + (3\pi WR)^2} \right]
\]  

(1.4)

Originally, Johnson et al. (eq. 1.4) considered the reversible elastic contact between two solids under equilibrium state, where \( G = W \). However, in practical cases, energy dissipation often occurs, which makes \( G \neq W \). For instance, energy may be dissipated in the viscoelastic and plastic deformation when the contact between two solids is not
purely elastic. Also interface reconstruction because of hydrogen-bonding or other interactions is often reported and can be strongly related to the contact conditions, such as the contact radius, external force applied, moisture, temperature, etc. Moreover, the contact between two solids is quite often not in equilibrium during measurements, which means the time scale employed in the measurements may greatly influence the obtained values. Therefore, the determination of the adhesion when energy dissipation occurs needs careful consideration. Since energy dissipation often takes place in practice, studying adhesion under such conditions is important.

The energy release rate, $G$, of the contact between two solids, for a purely elastic contact under equilibrium (JKR model), can be given by:

$$ G = G_{elas} = W $$

For contact where energy dissipation occurs,

$$ G = G_{elas} + G_{diss} $$

where $G_{elas}$ represents the strain energy release rate caused by purely elastic deformation, and $G_{diss}$ is the energy dissipation term.

In the literature, normally equation 1.1 and 1.4 are used to obtain values for $G$ and $W$. However, when the deformation is not purely elastic and/or equilibrium is not reached, the original JKR model is no longer valid. Many efforts have been made to modify the JKR model, for instance, for viscoelastic deformation [17-20]. Unfortunately so far no agreement has been obtained in this field, and equation 1.1 is generally used as the only approach by researchers to obtain meaningful values of $G$, when $G \neq W$. Values for $G$ are calculated according to equation 1.1 for every point along a loading as well as unloading curve of a JKR measurement.

Most processes involving adhesion and wetting are hysteretic. Hysteresis is a common occurrence with almost all types of practical interfacial phenomena [21-22]. For instance, in practical adhesion measurements, the work done on separating two surfaces from adhesive contact is generally much greater than the work delivered when the two surfaces are brought into contact. This difference is referred as adhesion hysteresis. Based on the calculated $G$ values, adhesion hysteresis is addressed by relating it to various possible mechanisms.

In this thesis, the same approach is applied. However, we fully realize that the calculated energy release rate values are the effective values which are approximations according to the JKR model. In order to clarify this, we use “$G_{eff}$” to represent the effective values calculated, from our experimental data, according to equation 1.1 throughout this thesis. Similarly, “$W_{eff}$”, “$K_{eff}$” and “$E_{eff}$” represent the calculated effective values according to equation 1.4. Adhesion hysteresis is expressed
as
\[ \Delta W = W_{ul}^{\text{eff}} - W_{l}^{\text{eff}} \] (1.5)

and
\[ \Delta G = G_{ul}^{\text{eff}} - G_{l}^{\text{eff}} \] (1.6)

where the subscripts of “ul” and “l” denote, respectively, the unloading (separating) and loading (approaching) part of the JKR measurement.

1.2.4. Basic materials in the thesis

In the literature on adhesion studies using the JKR technique, crosslinked poly(dimethylsiloxane) (PDMS) is the most frequently used material. This material was chosen as the basic starting material for this thesis for the following reasons: Firstly, crosslinked PDMS has excellent linear elasticity, a homogeneous and smooth surface and optical transparency, which makes it an attractive material for JKR experiments. Secondly, it is relatively easy to manipulate their bulk and surface properties by using commercially available starting materials. Thirdly, there are a large number of published data available on crosslinked PDMS using the JKR technique. This will make it easier to test the performance of the newly built JKR apparatus used in our study and to compare our measurements with literature data. Fourthly, the choice of PDMS offered the possibility to study the influences on adhesion, of such as submicrometer fillers, surface modification and thin top layers. These influences are also important under practical circumstances.

1.3. Objectives and the scope of the thesis

The topic of this thesis is the adhesion study of polymers. A newly built JKR apparatus is used, together with other techniques, such as contact angle and micro-indentation measurements, to determine the adhesion properties of PDMS based materials. Crosslinked PDMS is used as the starting model material. The influences of submicrometer fillers in PDMS, modification and application of thin layers on PDMS surfaces, are also studied. The main focus in this thesis is adhesion and adhesion hysteresis under non-equilibrium conditions.

The objectives of this thesis are (1) the design and construction of a JKR apparatus and testing of the reliability of this apparatus; (2) the study on the factors which affect the self-adhesion behavior of crosslinked PDMS materials; (3) the study, based on crosslinked PDMS materials, of the influences of submicrometer fillers, surface modification and thin top layers on the adhesion properties.

Chapter 2 gives a brief introduction on the JKR theory, apparatus and typical experiments conducted in our work. The accuracy and reliability of our newly built
apparatus will be proven. Micro-indentation and contact angle measurements are used to compare the elastic moduli and surface energies with values obtained with the JKR technique.

In Chapter 3, the reliability of the micro-indentation technique to determine the elastic moduli of crosslinked PDMS materials will be shown. Micro-indentation measurements will be used in other chapters to assess the reliability of the elastic modulus obtained with the JKR technique.

Chapter 4 presents an in-depth study on the self-adhesion property of crosslinked PDMS materials. The influence of several factors on the self-adhesion and adhesion hysteresis of these materials are investigated, such as molecular weights of the starting linear PDMS polymers, the bulk viscoelasticity, the presence of the sol fraction, the surface roughness, dangling chains, the use of crosslinker in excess in the initial formulation and the average molar mass between crosslinks in the final materials.

Chapter 5 deals with a study on the influence of submicrometer filler particles present at or close to the surface on the adhesion properties of crosslinked PDMS materials. The fillers are in-situ precipitated SiO\textsubscript{2} particles. Two types of surfaces are prepared for study: surfaces made in contact with air and made in contact with different substrates.

Chapter 6 focuses on the surface modification of PDMS, which is used frequently in practice to enhance adhesion. To study this, the surfaces of crosslinked PDMS are treated with UV/O\textsubscript{3} with different exposure times. The adhesion between these treated PDMS lenses and sheets of non-treated PDMS, polystyrene (PS) and indium tin oxide (ITO) is studied. Special attention will be given to the applicability of the JKR model for interpreting the experimental data.

In Chapter 7 an organic thin layer of polystyrene (PS) and an inorganic thin layer of indium tin oxide (ITO) are applied on the surface of crosslinked PDMS lenses. The usefulness of the application of the JKR technique to study the adhesion between these lenses and commercially attractive coating/(polymer) substrate will be discussed.

As an extension to Chapter 3, the application of micro-indentation on other crosslinked coatings is demonstrated in Chapter 8. Crosslinked coatings prepared from a linear telechelic carboxyl-terminated poly(butyl acrylate) with a narrow molecular weight distribution and a linear random co-polymers with about the same average functionality were chosen as model materials for this study.
References

Chapter 2

The JKR technique – theory, apparatus and experiments

2.1. Introduction

The JKR theory is a continuum contact mechanical theory developed by Johnson, Kendall, and Roberts [1]. It is an extension of the Hertz theory [2] by the introduction of adhesive forces operating at the interface between two linear elastic solids in contact. The JKR theory provides the analytical framework for measurements of the work of adhesion and interfacial energy via contact mechanics and is well-suited to analyse the contact at interfaces where at least one of the materials is relatively soft [3, 4].

For a purely elastic contact between two spherical solids at equilibrium, the JKR theory predicts that the radius of the contact area, \(a\), under an external force, \(P\), is related to the thermodynamic work of adhesion, \(W\), as follows [1]:

\[
a^3 = \frac{R}{K} \left[ P + 3\pi WR + \sqrt{6\pi WRP + (3\pi WR)^2} \right]
\]  

(1.4)

where

\[
\frac{1}{K} = \frac{3}{4} \left[ \frac{1-v_1^2}{E_1} + \frac{1-v_2^2}{E_2} \right]
\]  

(1.2)

\[
\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}
\]  

(1.3)

\(K\) is the elastic constant, \(R_1\) and \(R_2\) are the radii of curvature of the two spheres, \(v_1, v_2\) and \(E_1, E_2\) are the Poisson ratios and elastic moduli of the two spheres, respectively.

The JKR equation is easily modified for particular cases. For contact between a sphere and a flat plate (Figure 2.1), the radius of curvature of the flat plate is infinite, and \(R\) becomes the radius of curvature of the sphere.

For contact between two identical solids (self-adhesion test), \(K\) is given by

\[
K = \frac{2E}{3(1-v^2)}
\]  

(2.1)

The basic JKR experiment is to bring a spherical lens and a flat (or spherical) sample into contact and then to measure the resulting radius of contact area, \(a\), under controlled force, \(P\). By fitting \(a\) and \(P\) data to equation 2.1, one can independently obtain \(K\) and \(W\) for the two samples in contact. If the surface energies of both samples...
are known, the interfacial energy, $\gamma_{12}$, may be deduced according to equation 2.5 [5]

$$W = \gamma_1 + \gamma_2 - \gamma_{12}$$

(2.2)

When the two samples are made of the same material, $\gamma_{12}$ becomes zero, and $W$ is twice the surface energy of the samples ($W = 2\gamma_1 = 2\gamma_2$) [6].

![Figure 2.1. Schematic diagram of the JKR experiment with contact between a sphere and a flat sheet.](image)

The JKR technique has been widely used to directly estimate the surface energy and work of adhesion of many organic and inorganic surfaces [4, 7-14]. The JKR analysis is a linear elastic analysis, which means the volume under deformation is small, thus plastic and viscoelastic effects are neglected. The deformation is on the mesoscopic scale and normally a microscope is used to observe the contact area. Therefore, there are, in general, limitations to the materials, which can be studied with a JKR apparatus: firstly, at least one sample has to be soft; secondly, at least one sample has to be transparent or opaque. When two materials with higher moduli are studied, one can calculate the nondimensional Tabor parameter [15] to check if the JKR theory is valid according to the following equation

$$\mu \equiv \left( \frac{RW^2}{E_r^2 z_0} \right)^{\frac{1}{3}}$$

(2.3)

where $R$ is the radius of the curvature of the spherical sample, $W$ the work of adhesion, $z_0$ the effective range of action of the adhesive force (typically taken to be on the order of 0.3 to 0.5 nm) [16]. The reduced modulus, $E_r$, is given by

$$\frac{1}{E_r} = \frac{1-v_1^2}{E_1} + \frac{1-v_2^2}{E_2}$$

(2.4)

For two identical samples, $E_r$ is given by

$$\frac{1}{E_r} = \frac{2(1-v^2)}{E}$$

(2.5)

For $\mu > 5$, the JKR theory applies and for $\mu < 0.1$, the Derjaguin, Muller, and Toporov (DMT) theory [17] applies. In between, the transition between these two theories
occurs [18, 19]. We will not discuss the DMT and other theories in our study, as shown in the next paragraph, for our systems the JKR theory always applies.

Crosslinked polydimethysiloxanes (PDMS) materials have been widely used as ideal model systems for (self-)adhesion studies using the JKR technique [2, 4, 20-25], because of its excellent linear elasticity, homogeneous and smooth surface, optical transparency, easy synthesis and the possibility to manipulate the bulk and surface properties with relative ease. Therefore, crosslinked PDMS lenses and sheets were chosen as the starting materials to test our newly built JKR apparatus by measuring the self-adhesion property of these materials. The validity of applying the JKR theory for our crosslinked PDMS materials was checked by calculating the Tabor parameter using equation 2.6 and 2.8. We take \( E \) as 1 MPa, \( W \approx 44 \text{ mJ/m}^2 \), \( z_0 \) as 0.5 nm and \( R \sim 1.5 \text{ mm} \), yielding a Tabor parameter \( \mu \approx 3720 \gg 5 \). We concluded that the JKR theory is valid for our materials and measurements. In this chapter we present the results of the self-adhesion study of these materials using a newly built JKR apparatus.

### 2.2. Experimental

#### 2.2.1. The JKR apparatus

Our newly built JKR apparatus is shown schematically in Figure 2.2. This apparatus works in displacement-control mode. A hemispherical lens and a flat sheet sample are placed on two holders, respectively. The holder for the flat sheet sample is firmly fixed. The holder for the lens sample is attached to a leaf spring, which is capable of moving to the flat sheet in the horizontal direction under the control of the motor. An interferometer is used to monitor the displacement of the lens sample and the force applied to the leaf spring. The interferometer is chosen because of its capacity of monitoring minor changes of displacement accurately. The stiffness of the leaf spring used is 2.457 \( \mu \text{N/nm} \). The contact area between the lens and sheet sample is imaged with a CCD camera connected to a stereo microscope.

During the JKR experiments, the time, the displacement of the motor, the displacement of the lens sample, the force applied and the contact area are monitored using a custom software program written with Labview (National Instruments, USA). This software provides the ease and flexibility of setting and recording the experimental parameters. By doing this, a continuous loading/unloading or step-wise loading/unloading or a mix of these two can be chosen as needed. The whole apparatus is placed on a heavy table to minimize the influences of any possible vibration and noise. This apparatus does not allow measurements under special conditions, such as controlled humidity, temperature and gas flow.
2.2.2. Materials

Four linear α,ω-vinyl terminated PDMS polymers (ABCR, Germany) with molecular weights of 6000 (PDMS 6), 9400 (PDMS 9), 17200 (PDMS 17) and 28000 (PDMS 28), respectively, were used as the starting materials. Tetrakis(dimethylsiloxy)silane, which is a four functional crosslinker, was also obtained from ABCR, Germany. Cis-dichlorobis(diethyl sulfide)platinum(II) was used as the catalyst. This powder was obtained from Strem Chemicals. All materials were used as received. It was assumed that each PDMS chain and crosslinker molecule contains 2 and 4 reactive groups, respectively.

The PDMS lenses and sheets used in the JKR study were prepared using the hydrosilylation crosslinking reaction as shown in Scheme 1. Firstly, α,ω-vinyl terminated PDMS and the cross-linker were mixed at room temperature. To characterize the mixture the stoichiometric ratio of silane hydrogens to vinyl groups, the so-called H/V ratio, is used. Generally an H/V ratio of 1.6 was used for making PDMS lenses and sheets for our JKR experiments. This mixture was stirred for 10 min. Next the catalyst, first dissolved in toluene (0.0023g /ml), was added into the mixture (20 ppm) and stirred for another 5 min at room temperature. The final mixture was degassed in a vacuum desiccator for 3 min before further operation.

From this mixture, the PDMS lenses were prepared according to the method developed by Chaudhury et al. [4]. Droplets of this mixture were placed with a microsyringe onto a pretreated surface of a smooth glass slide [4] (see the next
paragraph for the pretreatment). Flat sheets of PDMS were prepared by pouring the mixture onto the same pretreated glass slides. All formulations were cured at 60 °C for 3 days under vacuum (~ 0.01 mbar). Side-view images were taken with the OCA30 apparatus (Dataphysics Instruments). The value of R was calculated from the heights (h) and basewidths (d₀) of the lenses (R = h/2 + d₀²/8h) as shown in Figure 2.3, assuming the lenses were perfectly hemispherically shaped. The radii of the curvature of the lenses, R, were in the range of 1 to 2 mm. The thickness of the sheets was about 1.5 mm.

The surface of the glass slide had been pretreated with 1H, 1H, 2H, 2H-prefluorodecyltrichlorosilane (ABCR, Germany) to lower the surface energy according to the following procedure. Glass slides were cleaned with ethanol in an ultrasonic bath for 5 min, rinsed with distilled water and dried at 120 °C in air, and then put in a UV/O₃ chamber for 15 min. The cleaned glass slides were dipped into a 2% solution of 1H, 1H, 2H, 2H-prefluorodecyltrichlorosilane in heptane for 12 hours. The slides were then rinsed with heptane several times, and heated at 90 °C under
vacuum (~ 0.01 mbar) to remove the unreacted silane molecules. The slides were then rinsed with methanol and dried in a dry nitrogen stream at room temperature. The fluoroalkylsilane-treated slides had two advantages: firstly, they provided a flat substrate from which the lenses could be removed easily after cure; secondly, the drops formed a finite angle of contact (ca. 66°) and the hemispherical shapes were kept after cure [4].

The commercial linear PDMS polymers used in our sample preparation had a relatively broad molecular weight distribution (MWD) (see Table 2.1). Hence, the optimum H/V ratio for network formation was determined by estimating the H/V ratio that corresponded to the crosslinked materials with the highest modulus and the lowest degree of equilibrium swelling [26]. To find this optimum H/V ratio, several crosslinked PDMS sheets from the mixture of PDMS 9, the crosslinker and the catalyst were prepared with different H/V ratios changing from 1.0 - 2.5.

2.2.3. Methods

2.2.3.1. Methods used other than JKR

The molecular weights and MWDs of the four α,ω-vinyl terminated PDMS were measured by size exclusion chromatography (SEC) using a Waters model 510 pump and a model 410 refractive-index detector (40 °C). Tetrahydrofuran (THF, Biosolve) was used as the eluent at a flow rate of 1.0 ml/min. Samples (1-2 mg/ml THF) were filtered through a 0.2 µm syringe filter prior to injection. Data acquisition and processing were performed using Waters Millennium 32 (v3.00) software. Calibration was done using polystyrene (PS) standards (Polymer Laboratories, 580 to 7.1 × 10^6 g mol⁻¹). Polystyrene-equivalent molecular weights are reported in this chapter.

Sol fractions and swelling ratios were obtained from the swelling experiments [27]. PDMS sheets were swollen in toluene to remove any impurities and soluble fractions. These sheets were swollen for 6 days, and the solvent was replaced with fresh toluene every day. Sheets were deswollen by adding methanol in 20% increments to the toluene bath over a period of 5 days. These samples were left in air at room temperature for solvent evaporation overnight, and then placed under vacuum (~ 0.01 mbar) at 60 °C for 12 h to remove the remaining solvents. The sol fraction (W_{sol}) and the swelling ratio (Q) of the sheets were computed from the following relationships:

\[
W_{sol} = \frac{M_0 - M_{ext}}{M_0} \times 100\% \tag{2.6}
\]

\[
Q = 1 + \frac{(M_{swo} - M_{ext}) \rho_2}{M_{ext} \rho_1} \tag{2.7}
\]

where \(M_0\) is the dry weight of the sheet before extraction, \(M_{ext}\) is the dry weight of the sheet after extraction, \(M_{swo}\) is the swollen weight (of the sheet and solvent combined),
and $\rho_1$ and $\rho_2$ are the densities of the solvent (0.867 g/ml for toluene) and polymer (0.96 g/ml for PDMS), respectively.

The elastic moduli of the PDMS flat sheets were measured with micro-indentation at room temperature using a home-built apparatus with a Berkovich type diamond indenter [28]. A loading force of 1-2 mN and a loading rate of 40 nm/s were selected for all measurements. The indentation displacements were in the range of 10-30 micrometer. More details about the determination of elastic moduli of crosslinked PDMS materials using micro-indentation will be presented in Chapter 3.

Transmission Fourier-Transform Infrared Spectroscopy (FT-IR) was performed using a Biorad UMA 500 infrared microscope coupled to a Biorad FTS 6000 FTIR spectrometer at room temperature. All spectra were recorded in-situ during curing in dry nitrogen at room temperature between 4000 and 400 cm$^{-1}$ with a resolution of 2 cm$^{-1}$ co-adding 50 scans. The band located at 1943 cm$^{-1}$ was found to be stable during cross-linking. All spectra were normalized by using this band as the internal standard [29]. The measurements were repeated at least once, and the differences between the recorded spectra appeared to be very small.

The surface morphology of the PDMS sheet samples was investigated using a Philips environmental scanning electron microscope XL-30 ESEM REG (Philips, now FEI Co., The Netherlands). Imaging of the sample surface was performed in the high-vacuum mode using acceleration voltages of 1 kV (low-voltage SEM, LVSEM) and a secondary electron (SE) detector.

The nanoscale surface roughness of the PDMS sheets and lenses were measured by using atomic force microscopy (AFM) (NTEGRA, NT-MTD, Moscow) in the intermittent contact mode with Si-cantilevers, spring constant $k = 5.5$ N/m (NSG01, NT-MDT, Moscow, Russia). In general, a sample area of $1 \times 1 \mu$m was scanned. The measurements were performed in air at room temperature at a humidity of 45-50%. The root mean square roughnesses were calculated from the AFM height images of the PDMS lenses and flat sheets.

Dynamic contact angles (DCA) analyses were performed in air at room temperature using the sessile drop method [30a] with the OCA30 apparatus (Dataphysics Instruments). Distilled water and methylene iodide (99.5+%, Aldrich) were used as the probe liquids. All advancing and receding contact angles were the average value of at least five measurements on different positions of the samples. The surface energies were calculated using the Owens-Wendt-Rabel-Kaelble (OWRK) method [30b] based on the advancing contact angles with water and methylene iodide.
2.2.3.2. JKR measurements

JKR experiments on non-extracted PDMS samples were conducted with a JKR apparatus, as described before. All measurements were conducted in air at room temperature with a humidity of 40 ~ 60%. Typically in our JKR experiments, a crosslinked PDMS lens was brought into contact with a crosslinked PDMS flat sheet made from the same formulation, in displacement control. Generally the experiments were carried out in a dynamic way – Loading and unloading experiments were conducted at a constant motor speed with variable waiting time at the peak load. The applied force was usually within the mN range, the indentation displacement of the sample was less than 25 µm, and the radius of the contact area was in the range of 50-200 µm. A typical example of an image of the contact area between a PDMS lens and a flat sheet measured with our JKR apparatus is given in Figure 2.4. A motor speed in the range of 50-500 nm/s was found to have only a small influence on the outcome of our JKR measurements for our crosslinked PDMS samples. To minimize the influence of the noise from outside, a motor speed of 100-200 nm/s was generally applied. The radii of the contact area, \( a \), were extracted from the microscopic images of the contact area using a software based on the Hough Transformation provided by TNO [31].

![Figure 2.4. Microscopic image of the contact area of a PDMS lens and a flat sheet (\( a = 130 \, \mu\text{m} \)).](image)

During a JKR experiment, the applied force, \( P \), the displacement of the sample, \( d \), and the images of the contact area were recorded with time. The original curves of force versus time showed a linear drift in the time scale we used for all measurements. This force drift is likely to be caused mainly by the thermo-expansion of the aluminium used for the construction of the apparatus. The variation of the temperature and/or pressure of the air and humidity will change the wavelength of the laser beam, and may also contribute to the drift of the force during measurements. This linear drift was corrected during data processing. The curves of force versus time for PDMS 28 samples before and after drift correction, with different waiting times, are given in Figure 2.5a. The drift was not a constant value, and could be different in the range of 0 ~ 0.5 µN/s. Repeated measurements, with different drift values, gave quite similar curves after drift correction (Figure 2.5b), and further data fitting gave very constant
values of \( W^{\text{eff}} \) and \( K^{\text{eff}} \) with a deviation of \( \sim 3 \% \). Therefore, the application of the linear drift correction on our data processing is very successful, and all discussions in the chapters of this thesis about our JKR experiments are based on drift correction data.

![Figure 2.5a](image1)

**Figure 2.5a.** Plots of force versus time before and after drift correction with different waiting time. Lens and sheet: non-extracted PDMS 28, motor speed: 200 nm/s

![Figure 2.5b](image2)

**Figure 2.5b.** Plots of force versus time before and after drift correction. Lens and sheet: non-extracted PDMS 28, motor speed: 200 nm/s, waiting time 15 min.

Typical curves of force (after correction), displacement and contact radius versus time in a loading – unloading cycle for the contact between a crosslinked PDMS lens and flat sheet are shown as figure 2.6 a, b and c, respectively. The loading part started at the “snap-on” point, which is visualized as a jump in both the force curve (figure 2.6a) and the displacement curve (figure 2.6b), whereas in the contact radius curve (figure 2.6c) it is the starting point. The displacement was kept constant during the waiting time at peak load, which resulted into a quite constant force and contact area. The unloading part started at the point where motor began to move in the reverse direction.
In the unloading part, the measured force decreased until it reached the “pull-off” force, and then increased and ended at the “snap-off” point, which is visualized again as a jump in the force and displacement curves and the last point of the radius curve. The “pull-off” force we defined, $P_{po}$, i.e. the maximum force needed to separate the contacting two samples, was always negative.

**Figure 2.6.** Typical curves of force (a), displacement (b) and contact radius (c) versus time in a loading-unloading cycle of the contact between non-extracted crosslinked PDMS 9 lens and sheet. Motor speed, 200 nm/s, waiting time: 60 s.
2.3. Results and discussions

2.3.1. Sample preparation and characterization

The molecular weights and MWDs of the four vinyl terminated linear PDMS polymers were determined with SEC (Table 2.1). The $M_n$ data obtained by us are in reasonable agreement with the data provided by the producer. All PDMS polymers have a relatively broad MWD (2.0 ~ 2.3).

| Table 2.1. Molecular weights and MWDs of the vinyl terminated PDMS polymers. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| PDMS 6          | 6000            | 5830            | 12030           | 2.1             |
| PDMS 9          | 9400            | 8940            | 17690           | 2.0             |
| PDMS 17         | 17200           | 16750           | 36170           | 2.2             |
| PDMS 28         | 28000           | 27300           | 64140           | 2.3             |
| *provided by ABCR, Germany.* |

To estimate the H/V ratio that corresponds to the samples with the highest modulus and lowest degree of equilibrium swelling, crosslinked PDMS 9 sheets were prepared using different H/V ratios between 1.0 and 2.5. The sol fractions, swelling ratios and elastic moduli measured of these PDMS 9 samples are given in Table 2.2. A ratio of 1.6 was found to produce the minimum sol fraction and swelling ratio, and the maximum elastic modulus. This is in agreement with the values of 1.4-1.7 reported for the optimum H/V ratio for very similar materials [26, 27]. Therefore an H/V ratio of 1.6 was chosen, as the optimum ratio, to prepare all the crosslinked PDMS lenses and sheets for the JKR study in this chapter.

| Table 2.2. Sol fractions, swelling ratios and elastic moduli of PMDS 9 elastomers prepared with different H/V molar ratios. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| H/V             | 1.0             | 1.3             | 1.6             | 1.9             | 2.2             | 2.5             |
| $W_{sol}$ %     | 4.9             | 2.9             | 2.8             | 3.4             | 4.7             | 6.8             |
| $Q$             | 4.77            | 3.64            | 3.55            | 3.75            | 4.12            | 5.16            |
| $E_{id}$ * MPa  | 0.84            | 1.00            | 1.04            | 0.97            | 0.91            | 0.79            |
| *measured using micro-indentation for samples before extraction.* |

The hydrosilylation reaction for PDMS 9 with the H/V ratio of 1.6 was followed using FT-IR. The band located at 2136 cm$^{-1}$ assigned to Si-H stretching [32, 33] does not interfere with any other band of the spectrum. Therefore, the change in the intensity of this band gives information about the crosslinking reaction shown in Scheme 1. This band was found to decrease with time and almost disappeared after cross-linking for 3 h at room temperature (Figure 2.7a). The absorption band at 1943 cm$^{-1}$ was found to
be stable during the reaction and was chosen as an internal reference to calculate the conversion rate of the Si-H group. The conversion rate of Si-H group reached a plateau of about 96% after curing for 1 h (Figure 2.7b), showing that not only the crosslinking reaction was (almost) complete, but also that (most of) the excess Si-H groups disappeared by side reactions.

![Graph showing absorbance and Si-H conversion over time](image)

**Figure 2.7.** Decrease of the absorption of Si-H stretching band (a) and conversion rate of the Si-H group (b) with time. Formulation: PDMS 9, H/V = 1.6.

### 2.3.2. Surface roughness of crosslinked PDMS materials

The application of the JKR theory requires smooth and homogeneous surfaces. Since the prepared crosslinked PDMS were used as model materials in our JKR study, the surface roughness of these PDMS networks is important.

![SEM image of a crosslinked PDMS 9 sheet](image)

**Figure 2.8.** SEM image of a crosslinked PDMS 9 sheet. The SEM image of a PDMS flat sheet was shown in Figure 2.8. The PDMS sheets were found to be smooth and homogeneous; no distinct features were observed from the SEM image.
AFM was used to measure the surface roughness of the PDMS sheet and lens samples at the nanometer scale. The height images of a PDMS sheet and lens were shown as Figure 2.9a and 2.9b, respectively. Both surfaces were smooth and homogeneous, giving similar root mean square roughness, $R_q$, of about 1 nm.

![AFM height images of a crosslinked PDMS 9 flat sheet (a) and a PDMS lens (b).](image)

**Figure 2.9.** AFM height images of a crosslinked PDMS 9 flat sheet (a) and a PDMS lens (b).

### 2.3.3. Results of the JKR study

![Typical curve of force versus displacement.](image)

**Figure 2.10.** Typical curve of force versus displacement.

Motor speed: 200 nm/s, waiting time: 5 s.

As explained before, during a JKR experiment, the applied force, $P$, the displacement of the sample, $d$, and the radius of the contact area, $a$, were recorded with time. Figure 2.10 showed a typical curve of force versus sample displacement for the contact between a PDMS 9 lens and a PDMS 9 sheet.
Figure 2.11. Typical curve of $a^3$ versus force.
Motor speed: 200 nm/s, waiting time: 5 s.

Figure 2.11 showed a typical curve of $a^3$ versus force for the contact between a PDMS 9 lens and a PDMS 9 sheet. The loading and unloading curves are very similar, and the unloading curve lies slightly above the loading curve. The slight difference between the loading and unloading curve in Figure 2.11 is an indication of adhesion hysteresis. It should be noticed that for zero force ($P = 0$), there is still a finite contact area ($a > 0$), as a consequence of surface forces. During unloading, contact remained ($a > 0$) and the force reduces to a negative value till snap-off occurs. All PDMS samples tested in this chapter showed a similar $a^3$ versus $P$ curves and little adhesion hysteresis.

The work of adhesion, $W_{l}^{\text{eff}}$ and the elastic constant $K_{l}^{\text{eff}}$ from the loading part of the $a^3$–$P$ curve were obtained by a two-parameter fit using equation 1.4 (Figure 2.12a). The elastic modulus $E_{l}^{\text{eff}}$ was calculated according to eq. 2.1. For the unloading curve, the $W_{ul}^{\text{eff}}$, $K_{ul}^{\text{eff}}$ and $E_{ul}^{\text{eff}}$ values can be determined using the same method as used for the loading curve (Figure 2.12b). It was found that $E_{ul}^{\text{eff}} = E_{l}^{\text{eff}}$ and $W_{ul}^{\text{eff}} > W_{l}^{\text{eff}}$. A small amount of hysteresis ($\Delta W = W_{ul}^{\text{eff}} - W_{l}^{\text{eff}}$) was thus observed.
Figure 2.12. Experimental data and fitted line of the loading curve (a) and unloading curve (b) of one JKR experiment. The tested samples were a non-extracted PDMS 9 lens and sheet (H/V = 1.6). Motor speed: 200 nm/s, waiting time: 5 s.

The strain energy release rate, $G$, during one cycle (loading and unloading) is given by the JKR theory:

$$G = \frac{\left(\frac{K a^3}{R} - P\right)^2}{6\pi K a^3}$$

(1.1)

where $K$ is taken as the value taken from the loading curve ($K_{eff}$ in our case). For perfectly reversible contacts and under equilibrium state, $G$ is equal to the thermodynamic work of adhesion, $W$. Practically when the contact is neither purely elastic (reversible), nor in a equilibrium state, equation 1.1 may be still used to calculate the effective strain energy release rate, $G_{eff}$. Frequently adhesion hysteresis, quantified by the difference between $G_{eff}$ ($W_{eff}$) values for unloading and loading curves, is observed.

The value of $G_{eff}$ was calculated, according to equation 1.1, for the same experimental data (Figure 2.12a and b) and plotted as a function of contact radius, $a$, as shown in Figure 2.12c. The $G_{eff}$ value was averaged to be 45 mJ/m$^2$, very close to 46.1 mJ/m$^2$ as obtained by the two-parameter fit shown in Figure 2.12b, and somewhat larger than $G_{eff}$ (~ 41 mJ/m$^2$) (see also Table 2.3).
All crosslinked PDMS materials tested here were found to have similar curves, showing only a small amount of hysteresis when a waiting time of 5 s was applied. Both the loading and unloading curves were fitted perfectly by the two-parameter fit. Figure 2.13 shows the plots of $a^3$ as a function of $P$ for the loading and unloading parts for PDMS 9 and PDMS 28.

According to the JKR model, from equation 1.4, there will only be real roots for the contact radius when:

$$P \geq -\frac{3\pi RW}{2}$$

(2.8)

Hence the "pull-off" force becomes
\[ P_{po} = -3\pi RW/2 \]  

(2.9)

and the "pull-off" adhesion, \( W_{po} \), is defined as:

\[ W_{po} = -2P_{po}/3\pi R \]  

(2.10)

\( W_{po}^{\text{eff}} \) values were also calculated according to equation 2.10 for our measurements and are given in Table 2.3. All data were averaged over at least three measurements on at least two different lenses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Loading</th>
<th>Unloading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( K_{\text{eff}}^{\text{eff}}, \text{MPa} )</td>
<td>( E_{\text{eff}}^{\text{eff}}, \text{MPa} )</td>
</tr>
<tr>
<td>PDMS 6</td>
<td>1.05±0.1</td>
<td>1.18±0.1</td>
</tr>
<tr>
<td>PDMS 9</td>
<td>0.90±0.1</td>
<td>1.01±0.1</td>
</tr>
<tr>
<td>PDMS 17</td>
<td>0.82±0.2</td>
<td>0.92±0.2</td>
</tr>
<tr>
<td>PDMS 28</td>
<td>0.71±0.1</td>
<td>0.80±0.1</td>
</tr>
</tbody>
</table>

* The ± sign indicates the sample standard deviation.

As is shown in Table 2.3, the elastic moduli decrease when increasing the molecular weight of the linear PDMS precursors. Fitting of both the loading and unloading curves gave the same elastic modulus for each lens and sheet combination.

The \( W_{i}^{\text{eff}} \) values are constant within the error of measurement for all PDMS samples studied here. The averaged value is 41.4 ± 1.0 mJ/m\(^2\). For these materials, according to equation 2.5 (\( W = 2\gamma \)), we calculated that for the loading part, the surface energy, \( \gamma \), is 20.7 ± 0.5 mJ/m\(^2\). This is in good agreement with literature data (20-22 mJ/m\(^2\)) [4, 13, 23].

\( W_{ul}^{\text{eff}} \) values were also found to be constant but slightly higher than \( W_{i}^{\text{eff}} \) values, suggesting a small amount of hysteresis. The surface energy obtained from the unloading data of our PDMS samples is averaged at 23.3 ± 0.6 mJ/m\(^2\), close to the range of 20-22 mJ/m\(^2\). \( W_{po}^{\text{eff}} \) values basically gave the same values as \( W_{ul}^{\text{eff}} \). An in-depth discussion about the observed adhesion hysteresis in these materials will be given in Chapter 4.

Micro-indentation and contact angle analysis were conducted to check the reliability of \( E_{i}^{\text{eff}} \) and \( \gamma_{JKR} \) values obtained from our JKR experiments. The results are listed in Table 2.4. The elastic moduli obtained from JKR and micro-indentation experiments were within the error of measurement equal.
Table 2.4. Comparison of the elastic moduli and the surface energies of non-extracted PDMS materials obtained using different techniques.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(E_i) (MPa)</th>
<th>(\gamma) ((\text{mJ/m}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS 6</td>
<td>1.18</td>
<td>21.0</td>
</tr>
<tr>
<td>PDMS 9</td>
<td>1.01</td>
<td>21.1</td>
</tr>
<tr>
<td>PDMS 17</td>
<td>0.92</td>
<td>21.7</td>
</tr>
<tr>
<td>PDMS 28</td>
<td>0.80</td>
<td>21.3</td>
</tr>
</tbody>
</table>

*\(E_i\) obtained by micro-indentation measurements.

\(\gamma\) calculated from the advancing contact angles with distilled water and methylene iodide.

All non-extracted crosslinked PDMS samples showed constant contact angles for the same probing liquid, with advancing contact angles \(\theta_a\) of ~ 106° and receding contact angles \(\theta_r\) of ~ 101° with water, and \(\theta_a\) of ~ 73° and \(\theta_r\) of ~ 68° with methylene iodide, respectively. Surface energies (\(\gamma_{CA}\)) were calculated from \(\theta_a\) data. As shown in Table 2.4, \(\gamma_{JKR}\) data calculated from the loading curves are in good agreement with our \(\gamma_{CA}\) values and literature data [4a, 34-36]. By comparing the \(E\) and \(\gamma\) values obtained from our JKR measurements and micro-indentation and contact angle measurements with literature data, we concluded that the results of our JKR experiments gave reliable data of \(E_i^{\text{eff}}\) and \(\gamma_{JKR}\) values. Therefore there experimental results confirmed the reliability of our newly built JKR apparatus in measuring the elastic modulus and work of adhesion of crosslinked elastic materials.

2.4. Conclusions

The design and construction of our newly built JKR apparatus was successful. It was capable of setting all experimental parameters in a convenient and flexible way.

Four non-extracted crosslinked PDMS materials were prepared and used as the testing materials for this JKR apparatus. These samples were quite suitable for the JKR testing, because of their homogeneous and smooth surface, their optical transparency and the amount of literature available on these materials.

The elastic moduli (\(E_i^{\text{eff}}\)) and the surface energies (\(\gamma_{JKR}\)) of our crosslinked PDMS materials were determined from the JKR experiments. These were compared with values obtained from micro-indentation and contact angle measurements, in order to check the reliability of our newly built JKR apparatus. The values of \(E_i^{\text{eff}}\) and \(\gamma_{JKR}\) measured with JKR experiments were found to be in very good agreement with values measured with micro-indentation and contact angle experiments, respectively, and also were in line with literature data. A more in-depth study on the self-adhesion of
crosslinked PDMS materials is presented in Chapter 4.

References


Chapter 3

Elastic moduli of crosslinked PDMS using Micro-indentation*

3.1. Introduction

In our mesoscopic study on the work of adhesion of crosslinked poly(dimethylsiloxane) (PDMS) materials using the Johnson-Kendall-Roberts (JKR) technique, as introduced in the previous chapter, the elastic modulus is a parameter of great importance. Conventional methods, such as dynamic mechanical analysis (DMA), encounter difficulties in determining the modulus of a rubber-like material with a very low glass transition temperature, $T_g$, coatings with thicknesses in the micrometer range and coatings on substrates. Hence, it is important and interesting to find another method to determine the elastic modulus of our crosslinked PDMS materials.

Depth sensing indentation (DSI) is widely used as a method to measure the mechanical properties of inorganic coatings. In the commonly used method developed by Oliver and Pharr [1], the elastic modulus and hardness can be determined on the basis of the experimental data for the indentation load, $P$, and displacement, $h$. The loading and unloading curve of $P-h$ is given in Figure 3.1 [1]. The tip-sample reduced modulus, $E_r$, is calculated using the following equation

$$E_r = \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}}$$

(3.1)

where $A$ is the contact area at full load, $S = dP/dh$ is the initial unloading stiffness, and $\beta$ is the geometry constant, equal to 1.034 for a Berkovich indenter [2]. The contact depth, $h_c$, is given as

$$h_c = h_{\text{max}} - \varepsilon \frac{P_{\text{max}}}{S}$$

(3.2)

where $\varepsilon$ is a constant, which equals to 0.75 for a Berkovich indenter. The contact area, $A$, for a Berkovich indenter with a perfect geometry, which is a three-sided pyramid with the inclination angle of 65.3° between the faces and the loading axis [3], is given as

$$A = 24.5h_c^2$$

(3.3)

* Part of this chapter has been published: Li, Z., Brokken-Zijp, J.C.M., de With, G., Polymer, 2004, 45, 5403.
Figure 3.1. Schematic representation of load $P$ versus indenter displacement $h$. (a) Initial surface; (b) surface profile after load removal; (c) indenter; (d) surface profile under load.

The reduced modulus is related to the elastic modulus of the material being tested by

$$\frac{1}{E_r} = \frac{1-v^2}{E} + \frac{1-v_i^2}{E_i}$$  \hspace{1cm} (3.4)

where $E$ and $v$ are the elastic modulus and Poisson’s ratio for the material, and $E_i$ and $v_i$ are the same parameters for the indenter. For a diamond indenter, the values of $E_i$ and $v_i$ are 1141 GPa and 0.07, respectively [4]. For perfect rubbery materials, Poisson’s ratio is taken as 0.5.

Recently the DSI technique is extended to polymer coatings/films [5-9]. So far there are only a few researchers [10-13] who applied DSI on rubber-like materials with a $T_g$ far below the room temperature. However, these researchers always found residual indentations indicating plastic deformation, whereas purely elastic behavior is expected. Furthermore, among their work, only Kaustubh Rau et al. [11] compared the modulus of the silicone thin film measured by DSI (3.72 ± 1.64 MPa) and DMA (8.65 ± 2.65 MPa), but their data are far from accurate. Therefore, how to make DSI a reliable technique for measuring the elastic modulus of a rubber-like coating/film is still a challenge.

DSI is called either as micro-indentation or nano-indentation when the indentation depth is in the micrometer or nanometer range. In this chapter, we used the micro-indentation technique to determine the elastic moduli of crosslinked PDMS flat sheets and coatings on PC substrates. To evaluate the reliability of this technique for
measuring the moduli of our samples, we compared the results obtained using micro-indentation with those of DMA for the same sheet samples. We also studied the maximum indentation displacement for measuring the elastic moduli of the coatings without seeing substrate effects.

3.2. Experimental

3.2.1. Materials

Vinyl-terminated poly(dimethylsiloxane) (PDMS 28, \(M_n = 28000\)) and the crosslinker were obtained from ABCR, Germany. Cis-dichlorobis(diethyl sulfide)platinum(II) (Strem Chemicals) was used as the catalyst. The crosslinker used in this chapter was a silane containing \(-\text{Si-H}\) groups with an average functionality of 10. All chemicals were used without further purification.

The crosslinked PDMS flat sheets and coatings on substrates used in this chapter were prepared by the hydrosilylation cross-linking reaction (see Chapter 2.2 for details). In general the mixture of PDMS 28, the cross-linker and the catalyst was applied onto a 3 mm thick commercial polycarbonate (PC) substrate (GE Plastic) using a coating applicator. Crosslinking was carried out at 60 °C for 3 days under vacuum (~ 0.01 mbar). Coatings with different thicknesses on PC substrate were prepared with a Si-H/Vinyl (H/V) ratio of 1.6. Each coating was cut to 1 cm \(\times\) 1 cm samples. The thickness of each coating was measured by optical microscopy through observing the cross-section of the coating/PC substrate. The thickness decreased by about 40 % after crosslinking.

Flat sheets with a thickness of 1 mm were also made using the abovementioned procedure. An H/V ratio in the range of 1.0 ~ 2.0 was used to prepare these sheet samples.

3.2.2. Methods

Micro-indentation experiments were carried out on all crosslinked PDMS 28 coatings and sheets in air at room temperature using a home-built apparatus with a Berkovich type diamond indenter. This apparatus allows experiments under displacement control to be performed only. The compliance of this system was 0.3 nm/mN and the contact area was related to the contact depth of the indentation by \(A = ah_c^2 + bh_c\) (\(a = 24.5\) and \(b = 5.71 \ \mu\text{m}\)) with \(h_c\) given in \(\mu\text{m}\). The apparatus and calibration procedure were introduced elsewhere [7-8]. To measure our crosslinked PDMS sheets and coatings, a loading rate of 40 nm/s was used and each indentation experiment was finished within 15 min. The indentation displacement observed was over several tens of micrometer when a load of several mN was applied. Measurements were conducted 3 times at each load on different places of one sample.
DMA experiments were conducted on 1 mm thick crosslinked PDMS 28 sheets prepared using different H/V values. The elastic moduli were measured in air at room temperature using a Rheometrics Solid Analyzer RSA-II in a time-sweep experiment in the uniaxial tension mode. All experiments were done with a frequency of 40 rad/s and a strain of 1%.

### 3.3. Results and discussion

#### 3.3.1. The reliability of micro-indentation in determination of elastic modulus

Indentations on PDMS 28 sheets prepared using different H/V ratios gave very similar curves of load force, $P$, versus displacement, $h$. An example is shown in Fig. 3.2. The unloading curve traced the loading curve perfectly within experimental error, showing that the contact between the indenter and film was purely elastic. After indentation experiments the testing area was observed by both optical microscopy and confocal microscopy and no imprint was found. This behavior was observed for all PDMS 28 sheets studied. Theoretically this phenomenon is expected for elastic materials, however, in practice some residual indentation depths and observable hysteresis between loading and unloading curves are always found in the literature [10-12]. The reasons for this observation may be the viscoelasticity of the samples and/or the effect of substrates.

![Figure 3.2](image)

**Figure 3.2.** A typical curve of indentation load $P$ versus indentation displacement $h$.

Sample: 1 mm thick crosslinked PDMS 28 sheet, H/V=1.6.

The reduced modulus was obtained by fitting the complete unloading curve instead of the initial unloading part, since the displacement was fully elastic. The elastic moduli were calculated, assuming Poisson’s ratio to be 0.5 for crosslinked PDMS materials. The calculated values of the elastic moduli of 1 mm thick PDMS 28 sheets with different H/V values are shown in Fig. 3.3. The sheets were measured with a loading range of 1-4 mN and the deviation of the calculated elastic moduli for the various
Elastic moduli of crosslinked PDMS using micro-indentation

loading ranges was less than 4.5%. Figure 3.3 shows that the elastic moduli increased with increasing the H/V value, and became almost constant at an H/V value around 1.6. Such a high H/V value ensures an optimum cross-linking as discussed in Chapter 2.3.

![Graph showing elastic moduli of crosslinked PDMS](image)

**Figure 3.3.** Elastic moduli of 1 mm thick PDMS 28 sheets determined with micro-indentation. Sheets were made using different H/V values.

The elastic moduli of the same sheets measured with micro-indentation and DMA are listed in Table 1. The values obtained by these two methods generally agree within 5%, proving the reliability of the values obtained by micro-indentation.

<table>
<thead>
<tr>
<th>H/V</th>
<th>E, MPa (Micro-indentation)</th>
<th>E, MPa (DMA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.575</td>
<td>0.550</td>
</tr>
<tr>
<td>1.2</td>
<td>0.809</td>
<td>0.795</td>
</tr>
<tr>
<td>1.4</td>
<td>0.901</td>
<td>0.858</td>
</tr>
<tr>
<td>1.6</td>
<td>0.942</td>
<td>0.941</td>
</tr>
<tr>
<td>2.0</td>
<td>0.970</td>
<td>0.955</td>
</tr>
</tbody>
</table>

In chapter 2 we present the moduli of PDMS 9 samples prepared with different H/V ratios and found that the moduli reached the maximum value when an H/V = 1.6 was applied. However, we found that for PDMS 28 samples studied here, an H/V = 2.0 gave a slightly higher modulus value than a sample prepared with H/V = 1.6. We attribute this small difference to the use of another crosslinker in the sample preparation. In this chapter a crosslinker containing Si-H groups with an average functionality of 10 was used, whereas in chapter 2 the crosslinker has a functionality of 4. Hence, the optimum H/V ratio may be different.

### 3.3.2. Effect of substrate

The $P-h$ curves of the PC substrate, crosslinked PDMS 28 coatings with different
thicknesses on the PC substrate and 1 mm PDMS 28 sheet (H/V=1.6) are shown in Fig. 3.4. The elastic modulus of PC measured was ~ 2.5 GPa. When the indentation displacements are less than about 10% of the coatings’ thickness, the $P-h$ curves follow the same trace, indicating no substrate effects within this range of depth. For a coating of 18 $\mu$m thickness, the effect of the substrate is obvious. At a penetration depth of about 3 $\mu$m, the loading curve and unloading curve do no longer match and the response of the PC substrate is observed. As the thickness of the coating increases, the effect of the substrate decreases gradually. The curve of 1.45 mm thick coating totally overlaps with the curve of 1 mm sheet sample.

The calculated reduced modulus, $E_r$, is plotted as a function of $h/h_t$ in Figure 3.5, where $h$ is the indentation displacement and $h_t$ is the total thickness of coating. The $E_r$ values seem to be quite constant when the indentation displacement is less than 10% of the thickness of the coating. When $h/h_t$ is larger than 10%, the calculated $E_r$ increases with an increase in $h/h_t$, indicating the effect of the PC substrate. In the literature, a conservative estimate on the maximum displacement, to which a film could be indented without seeing substrate effects, is below 10% [14-16]. This value can be different when different coating/substrate systems are tested. Cai and Bangert [17] found no substrate effect up to 33% depth for a soft metal on silicon substrate, but, 7% for a hard film on soft substrate. In the case of an elastic coating, some studies reported that indentation could be performed within the full thickness of the coating [10] or an S-shape behavior [8]. Clifford et al. [18] showed, using finite element analysis, that the 10% rule is invalid for coating thickness below 5 $\mu$m and proposed a new rule which depends on the coating thickness. Our results showed that the substrate effects are minimal as long as the indentation displacement is below 10% of the total thickness of the crosslinked PDMS coating.

![Figure 3.4. $P$ versus $h$ curves of the PC, crosslinked PDMS 28 coating with different thicknesses on PC substrates and 1 mm thick PDMS 28 sheet. H/V=1.6.](image)

Chapter 3
Elastic moduli of crosslinked PDMS using micro-indentation

Figure 3.5. Plot of $E_r$ versus the ratio of the displacement and the total thickness of coating ($h/h_t$) for crosslinked PDMS 28 coatings with different thicknesses on PC substrates. H/V=1.6.

3.4. Conclusions

In this chapter we have used the micro-indentation technique to measure the elastic moduli of the silicone rubber coatings on substrates and freestanding silicone rubber films at micro-penetration depth. Complete elastic behavior for rubber-like films was observed for all sheet samples. The calculated elastic moduli of the crosslinked PDMS sheets from the micro-indentation measurements are in good agreement with those measured by DMA. The PC substrate appeared to have no effects on the measured moduli of PDMS coatings when the indentation displacement was less than 10% of the total coating thickness. Our results showed that the micro-indentation technique is a reliable and convenient tool for an accurate estimation of the elastic modulus of a rubber-like sheet and coating on a substrate.

References


Chapter 4

Self-adhesion study on crosslinked PDMS

4.1. Introduction

Since their introduction in the 1960’s, polysiloxanes, or silicone rubbers as they also called, have steadily gained market share from porcelain and glass as outdoor insulation and protective materials due to their low weight, good electrical properties, hydrophobic surface properties and elastic properties over a large range of temperatures ($T_g \sim -120 ^\circ C$) [1-3]. The silicone rubber used in these applications is almost exclusively based on poly(dimethyl siloxane) (PDMS). PDMS has a very low surface-energy pendant group (the –CH$_3$ group) that is arranged along the highly flexible siloxane chain (–Si–O–) [4]. Its unique surface (interfacial) properties have been attributed to the low intermolecular forces between the methyl groups, the flexibility of the siloxane backbone, the partial ionic nature of the siloxane bond, and the high bond energy of the siloxane bond [5]. These surface (interfacial) properties, its mechanical and electrical properties and its long term stability, give PDMS wide and special applications for insulation [6], anticorrosion, antifouling [7], soft lithography [8], photo-finishing [9-11] and biomedical practice [12-15].

It is of great interest and importance for many applications to tailor the microstructure of the surface of PDMS, so that either good or bad adhesion can be obtained. Therefore, it is necessary to understand the adhesion properties of these materials in depth. As a commonly used model material for the JKR technique, the adhesion properties of crosslinked PDMS have been investigated by a number of researchers in the past two decades [16-23]. In 1991, Chaudhury and Whitesides [16] developed a very simple method for making spherical crosslinked PDMS lenses and directly measured the adhesion by using a home-built apparatus. Their pioneering work provided a convenient route for the direct measurement of adhesion between two samples. In the JKR experiments, the two solids tested can be either identical, i.e. so-called self-adhesion test, or different.

In many adhesion processes, the work done on separating two surfaces from adhesive contact is larger than that released when these surfaces come into contact. This
difference, called adhesion hysteresis, is common with most practical interfacial phenomena, such as wetting [17]. In JKR experiments, very often a substantial adhesion hysteresis is observed during a loading-unloading cycle. This hysteresis manifests itself as a difference between the loading and unloading curves, whereas the JKR model predicts that the unloading and loading curves should superimpose. In adhesion experiments, hysteresis indicates the occurrence of some irreversible transformation or metastable states on contact. As suggested by Israelachvili [18], when using the JKR technique, a mechanical hysteresis always takes place. When two surfaces are brought towards each other, a spontaneous jump (snap-in) occurs at some point establishing a finite contact area even at zero applied load. This jump is the manifestation of the interaction between the surfaces. Likewise, on separation from adhesion contact, there will also be a spontaneous jump (snap-off). Due to these mechanical instabilities, the process cannot be reversible in a thermodynamic sense, and the work of adhesion needed to separate the surfaces from contact must be greater than that on approach. But such mechanical hysteresis will not occur if the attractive forces are weak or if the backing material supporting the surfaces is very rigid. If the cycle were to be carried out infinitely slowly, the process should be reversible.

The origin of adhesion hysteresis is not always understood, sometimes controversial, and may well be different for different situations [19]. Adhesion hysteresis may be the result of chemical bond formation in the contact area [20, 21], surface rearrangement or reconstruction of molecular groups at the interface [21, 22], chain interdigitation and entanglements across the interface [23-26], bulk viscoelasticity of the contacting materials [27-29], surface roughness or heterogeneity [30-32], and the action of capillary forces [33]. In practically used adhesion systems, these effects are usually coupled. This combination of these effects makes it difficult to interpret the adhesion hysteresis.

Many efforts have been made to decouple sources of hysteresis by using homogeneous model surfaces. Several authors have investigated the self-adhesion of crosslinked PDMS, among them some have reported the occurrence of self-adhesion hysteresis during unloading [19-21, 24-29]. It is interesting to notice that self-hysteresis was observed, in most of the cases, after the crosslinked PDMS samples were extracted with a good solvent. It was attributed to several hysteresis sources as described below.

Silberzan et al. [20] prepared crosslinked PDMS from commercial linear PDMS
Self-adhesion study on crosslinked PDMS materials using an excess of cross-linker. They observed, in self-adhesion experiments, hysteresis already before extraction. When using extracted materials, the hysteresis became much larger. They believed that the hysteresis resulted from the excess Si-H groups being oxidized to Si–OH, which can form hydrogen bonds across the interface. Perutz et al. [21] claimed that the adhesion hysteresis they observed arised from a surface reconstruction reaction between Si–OH groups. After crosslinked PDMS samples were hydrolyzed in 0.1 M HCl aqueous solution, the hysteresis was found to increase strongly with hydrolysis time. By reaction of the hydrolyzed PDMS with hexamethyldisilazane to chemically mask the Si-OH groups, the hysteresis decreased significantly.

Perutz et al. [34] also prepared model crosslinked PDMS materials with controlled excess amounts of crosslinker. In their systems, when no excess crosslinker was added, little or no hysteresis was found for both before and after extraction. The hysteresis before and after extraction was found to increase with the amounts of crosslinker in excess added. By poisoning the platinum complex catalyst with a thiol, the hysteresis could be significantly lowered. Therefore, they believed that the hysteresis stemmed from a complexation between the excess crosslinker and the catalyst. The unloading rate dependency of this chemical adhesion hysteresis was attributed to the rate of bond dissociation of this complex. Emerson et al. [35] removed the unreacted Si-H groups in their systems by reaction with ethylene gas, but still observed hysteresis. In this way they showed that the presence of Si-H groups is not required for hysteresis to occur between extracted crosslinked PDMS materials.

Choi et al. [26] observed self-adhesion hysteresis only in extracted crosslinked PDMS materials. They prepared different PDMS samples by changing the crosslinker to PDMS ratio. They argued that the entanglement of tethered chains and their interdigitation with the extracted cross-linked PDMS at the interface might be the dominating mechanisms for the observed adhesion hysteresis. It was shown that the amount of extracted sol fraction was a function of the crosslinker to PDMS polymer ratio, and was also correlated with the amount of hysteresis. Entanglement of chains across the interface was also given as the source of hysteresis by Amouroux et al. [29]. They studied model crosslinked PDMS with controlled amounts of dangling chains. The hysteresis was found to be time dependent, and to increase with the amount of dangling chains. They believed that this hysteresis originated from the progressive bridging of the interface by pendant chains present in the network. According to their experimental data, viscoelastic effects might also be the origin of the adhesion
hysteresis. Mason et al. [36] reported that self-adhesion hysteresis was only observed after extraction for crosslinked PDMS with a high molecular weight between crosslinks, while more tightly crosslinked PDMS did not display self-adhesion hysteresis even at extended contact time under load.

Several researchers have studied the efficiency of dangling chains acting as connector molecules to promote adhesion at the interface between a crosslinked network and a rigid surface grafted with a polymer molecule layer. De Gennes and co-workers [37, 38] predicted a relationship between the adhesion hysteresis and the polymerization index and the areal density of connector chains under equilibrium conditions. Their results show the importance of the influence of the molecular weigh of the connector chains at the interface and their ability to interdiffuse or interpenetrate across the interface.

Many researchers have investigated the adhesion hysteresis caused by chemical bridging, namely, primary or secondary bonds formed at the interface during the time of contact [16, 20, 39]. A widely used method is to chemically modify the surface of crosslinked PDMS by introducing the functional groups of interest, or to use self-assembled model surfaces containing different chemical functionalities. Hysteresis may originate from the non-specific (van der Waals, dipolar) and specific (donor-acceptor, H-bond, acid-base) interactions [39].

In this chapter, we mainly address the self-adhesion of crosslinked PDMS materials by using the same JKR apparatus which was described in Chapter 2. We carried out a study on the influences of molecular weight of the starting linear PDMS polymers, the bulk viscoelasticity, the sol fraction, the surface roughness, dangling chains, the use of crosslinker in excess and the average molar mass between crosslinks on the self-adhesion and adhesion hysteresis of our materials. These factors will be discussed in the Results and discussion part of this chapter, as is shown in Scheme 4.1.
4.2. Experimental

4.2.1. Materials

Crosslinked PDMS lenses and sheets for the JKR study were prepared by hydrosilylation (Scheme 1, Chapter 2) according to the procedure described in Chapter 2.2.2. Four linear PDMS polymers with different molecular weights were used as the starting materials. As is shown in the previous chapter, the prepared crosslinked PDMS had the lowest sol fraction and highest elastic modulus when the molar ratio of Si-H to vinyl groups (H/V) was 1.6. Therefore, the H/V = 1.6 was chosen for the preparation of most of our PDMS samples. Solvent extraction was conducted according to the procedure in Chapter 2.2.3. Sol fractions of these samples were found to be less than 3%.

An H/V ratio of 2.5 was also applied to prepare crosslinked PDMS 9 lenses and sheets. These samples, together with PDMS 9 samples prepared with an H/V ratio of 1.6, were extracted with toluene and 1-dodecanethiol (~300 ppm) was added to the last bath of toluene to poison the Pt catalyst [34].

To obtain crosslinked PDMS samples with a certain amount of dangling chains but identical chemistry (i.e., the same H/V ratio), some quantities of pentamethyldisiloxane (MM$_H$, Sigma Aldrich) were added in the reaction mixture [29], as shown in Scheme 4.2. The unique SiH end of this molecule reacts with one vinyl end group of a PDMS chain, giving a dangling chain (provided the other end of this
The main parameters for the sample preparation and sol fractions of crosslinked PDMS sheets are given in Table 4.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$</th>
<th>H/V</th>
<th>MM$^H$/SiH</th>
<th>Sol fraction, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS 6</td>
<td>6000</td>
<td>1.6</td>
<td>0</td>
<td>2.52</td>
</tr>
<tr>
<td>PDMS 9</td>
<td>9400</td>
<td>1.6</td>
<td>0</td>
<td>2.84</td>
</tr>
<tr>
<td>PDMS 9 (H/V=2.5)</td>
<td>9400</td>
<td>2.5</td>
<td>0</td>
<td>6.81</td>
</tr>
<tr>
<td>PDMS 17</td>
<td>17200</td>
<td>1.6</td>
<td>0</td>
<td>2.93</td>
</tr>
<tr>
<td>PDMS 28</td>
<td>28000</td>
<td>1.6</td>
<td>0</td>
<td>2.68</td>
</tr>
<tr>
<td>PDMS 6-MM$^H$25</td>
<td>6000</td>
<td>1.6</td>
<td>0.25</td>
<td>9.25</td>
</tr>
<tr>
<td>PDMS 6-MM$^H$33</td>
<td>6000</td>
<td>1.6</td>
<td>0.33</td>
<td>15.40</td>
</tr>
<tr>
<td>PDMS 17-MM$^H$25</td>
<td>17200</td>
<td>1.6</td>
<td>0.25</td>
<td>8.31</td>
</tr>
</tbody>
</table>

A polystyrene (PS) coating and a clean silicon wafer were prepared for contact angle measurements as follows. PS (Polymer standards) was dissolved in toluene to make a 2 wt % solution. This solution was filtered using a 0.2 µm Millipore filter and spin-coated on a silicon wafer. A piece of a new silicon wafer (Sigma Aldrich) was cleaned in an ultrasonic bath of methanol for 5 min and washed with distilled water, finally put in an UV/O$_3$ chamber (PR-100 UV-Ozone Photoreactor) to treat the surface for 15 min.
4.2.2. Methods
Self-adhesion experiments were conducted on these crosslinked PDMS samples with our newly built JKR apparatus according to the procedure described in Chapter 2. A motor speed of 200 nm/s was applied in all experiments unless mentioned otherwise. All samples were measured at least three times. Different waiting times between the loading and unloading parts were applied to study the effect on adhesion hysteresis in relation to increasing contact times.

Dynamic contact angles (DCA) analyses, atomic force microscopy (AFM) and Transmission fourier-transform infrared (FT-IR) were performed according to the procedures described in Chapter 2.2.3.

4.3. Results and discussion

4.3.1. Influence of molecular weights ($M_n$) of starting linear PDMS polymers
For an ideal crosslinked polymer material made with no defects (i.e. unreacted groups and/or dangling chains), the molecular weight ($M_n$) of the starting linear polymers is (almost) identical to the molecular weight of the chain between crosslinks.

That adhesion is related to the polymer molecular weight between crosslinks has been known for some time [40-42]. De Gennes et al. [43] showed with their model that, for a close contact between a rubber and a solid surface, the energy release rate $G$, in the limit of zero crack propagation velocity, is given by $G \approx WN_0^{0.5}$, where $N_0$ is the number of monomers between crosslinks in the networks. This model also showed that $G$ is always larger than the thermodynamic work of adhesion, $W$, because of irreversible processes near the rubber-solid interface. Choi and co-workers [44] confirmed this relation by studying the adhesion of extracted crosslinked PDMS networks to a silicon oxide surface. On the other hand, self-adhesion studies on the same crosslinked PDMS networks resulted in the same value for the work of adhesion ($\sim 42$ mJ/m$^2$), showing no molecular weight dependence [45]. Hence, we decided to study the effect of $M_n$ of linear PDMS polymers on self-adhesion properties of crosslinked PDMS materials.

In principle, by end-linking linear vinyl-terminated PDMS chains via the hydrosilylation reaction, the network structure is well-controlled by the molecular weight and the molecular weight distribution of the starting PDMS chains before
crosslinking, because of the high selectivity of the reaction between the vinyl group
and SiH group [46]. The results of the JKR measurements on the crosslinked PDMS
materials prepared from linear polymers with different $M_n$ are shown in Figure 4.1
and Table 4.2. As introduced in Chapter 2.3.3, the elastic moduli and work of
adhesion were calculated using the loading and unloading data according to equation
1.4 and 2.1. Values with the subscript “l” and “ul” are denoted as values obtained
from the loading and unloading curves, respectively.

Table 4.2. JKR results of non-extracted crosslinked PDMS prepared from linear
polymers with different $M_n^*$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$</th>
<th>$E_{eff}$, MPa</th>
<th>$W_{l}^{eff}$, mJ/m$^2$</th>
<th>$E_{eff}$, MPa</th>
<th>$W_{ul}^{eff}$, mJ/m$^2$</th>
<th>$W_{po}^{eff}$, mJ/m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS 6</td>
<td>6000</td>
<td>1.18</td>
<td>42.2</td>
<td>1.19</td>
<td>45.7</td>
<td>45.9</td>
</tr>
<tr>
<td>PDMS 9</td>
<td>9400</td>
<td>1.01</td>
<td>41.8</td>
<td>1.00</td>
<td>46.0</td>
<td>45.2</td>
</tr>
<tr>
<td>PDMS 17</td>
<td>17200</td>
<td>0.92</td>
<td>40.4</td>
<td>0.91</td>
<td>46.4</td>
<td>45.3</td>
</tr>
<tr>
<td>PDMS 28</td>
<td>28000</td>
<td>0.80</td>
<td>41.2</td>
<td>0.81</td>
<td>48.6</td>
<td>46.1</td>
</tr>
</tbody>
</table>

* measured at a motor speed of 200 nm/s, waiting time: 5 s.

All data shown were tested at a fixed loading-unloading motor speed (200 nm/s) and
the waiting times were kept constant (5 s). For the non-extracted PDMS samples, the
curves of $a^3$ versus $P$ and the effective energy release rates, $G_{eff}$, calculated according
to equation 1.1, as the function of contact radius, $a$, are shown Figure 4.1.

All samples were found to have constant $W_{l}^{eff}$ and $W_{ul}^{eff}$ values of ~ 41 mJ/m$^2$ and ~
46 mJ/m$^2$, respectively. The surface energies obtained from the $W^{eff}$ values ($= 2\gamma$)
were ~ 20.5 mJ/m$^2$ and ~ 23 mJ/m$^2$ for loading and unloading data, respectively, in
agreement with the value reported in the literature [16, 21, 26, 29] and our contact
angle results (Chapter 2). These two values were found to be equal within the error of
measurement (± 5%) and are rather constant for all samples measured. They appeared
to be independent of motor speed in a range of 100-500 nm/s were applied. This
motor speed range of 100-500 nm/s generally gave an unloading rate, $V = -da/dt$, of ~
0.5-2.5 µm/s.
As shown in Figure 4.1b, a constant adhesion hysteresis of ~ 12% was observed for all samples when a waiting time of 5 s was applied. Many researchers have shown that it is always necessary to consider bulk viscoelastic losses when interpreting the adhesion hysteresis of a material [27-29]. Experiments indicate that the thermodynamic work of adhesion, \( W \), needs to be is multiplied by a temperature- and rate-dependent factor \( \Phi(V, T) \), to explain the measured hysteresis as shown in equation 4.1 [47]

\[
G - W = W \Phi(V, T)
\] (4.1)

where \( G \) is the measured energy release rate at the crack tip (\( G = G^{\text{eff}} \) in our cases ). \( \Phi \) is the viscoelastic amplification factor which will become smaller at smaller crack propagation rate. When \( V \) is very low, energy dissipation in the materials because of viscoelastic losses close to the crack tip should be negligible, therefore \( G^{\text{eff}} \approx W \). At a finite loading/unloading rate, the measured \( G^{\text{eff}} \) value can be much higher than \( W \) if \( \Phi \) is not negligible.

For “perfect” crosslinked PDMS networks, a relaxation time in the range of several tens of seconds to a couple of minutes have been reported in the literature [26, 45]. Therefore, it is very likely that the bulk viscoelastic losses will play a role when the experimental time scale is comparable with the relaxation time of our materials. To
check if the observed hysteresis in our samples can be attributed to the bulk viscoelastic losses, we conducted a comparable JKR experiment on the same sample (PDMS 17) with a motor speed of 200 nm/s and 20 nm/s with the same waiting time of 5 s. These two motor speeds gave a detachment rate of 1 µm/s and 0.1 µm/s, respectively. The plots of $a^3 - P$ and $G^{eff} - a$ are shown Figure 4.2 and Figure 4.3, respectively. The $a^3 - P$ and $G^{eff} - a$ curves at 20 nm/s were found to fall somewhere between the loading and unloading curves at 200 nm/s, showing that the hysteresis decreased when a slower crack propagation rate was applied. The loading and unloading curves tested at 20 nm/s showed hardly any hysteresis, giving an averaged $G^{eff}$ value of $\sim$ 43 mJ/m$^2$ for both loading and unloading curve.

![Figure 4.2. Plot of $a^3$ versus $P$ for PDMS 17 tested at different motor speeds.](image)

![Figure 4.3. Plot of $G^{eff}$ versus $a$ for PDMS 17 tested at different motor speeds.](image)
The difference observed above is also shown in the plots of force and contact radius versus time (Figure 4.4). For a motor speed of 200 nm/s, a discrepancy between the time at maximum force \( (P) \) and maximum contact radius \( (a) \) was observed, namely, the contact radius was not the maximum when the force reached its maximum.

![Figure 4.4. Plots of \( P \) and \( a \) versus time for crosslinked PDMS 17 when tested at 200 nm/s (a) and 20 nm/s (b).](image)

However, when a motor speed of 20 nm/s was applied, this discrepancy almost disappeared, and the recorded force and the contact radius reached the maximum values at the same time. Therefore we conclude that the contact between the lens and sheet is very close to the equilibrium state when a loading/unloading rate as low as 0.1 \( \mu \)m/s is applied. The \( G_{\text{eff}} \) value of \( \sim 43 \text{ mJ/m}^2 \) can be regarded as the thermodynamic work of adhesion, \( W \), for all crosslinked PDMS materials studied in this section.

Based on the above discussions, we can conclude that the observed self-adhesion hysteresis in PDMS 17 samples measured at 200 nm/s (Table 4.2) originates from bulk viscoelastic losses. This contribution disappears when a much lower loading/unloading rate is applied. According to equation 4.1, \( \Phi \) is calculated to be about 0.12 for our experiments when a motor speed range of about 200 nm/s and a waiting time of 5 s were applied. This value is comparable with literature data for similar materials [29].

We also performed experiments with a waiting time of 15 min for all the samples in Table 4.2. As shown in Figure 4.5, an effect of waiting time was only observed for sample PDMS 28 (which will be discussed in 4.3.2). This independency of waiting time confirms that the observed adhesion hysteresis in PDMS 6, PDMS 9 and PDMS
17 can be explained by bulk viscoelastic losses caused by the chosen measurement conditions. Although, in principle, additive rule cannot be applied quantitatively for adhesion hysteresis contributions of different sources, we assume in the next part of this chapter, that a difference between $G^\text{eff}_l$ and $G^\text{eff}_u$ larger than 12% under the same measurement conditions as mentioned above, must be (partly) attributed to other factors than the bulk viscoelastic losses when the observed hysteresis appeared also to be dependent on waiting times.

**Figure 4.5.** Plot of $G^\text{eff}$ versus $a$ with different waiting times for non-extracted crosslinked PDMS 6, PDMS 9, PDMS 17 and PDMS 28. Motor speed: 200 nm/s.

It is also interesting to see that the calculated elastic moduli $E^\text{eff}_l$ and $E^\text{eff}_u$ are always equal for the materials tested (see Table 4.2). For the experiments shown in Figure 4.2, $E^\text{eff}_l$ and $E^\text{eff}_u$ values are, contrary to the $W^\text{eff}_l$ and $W^\text{eff}_u$ values, not dependent on the loading/unloading rates, indicating their “true” elastic character.
4.3.2. Influence of the extraction of the sol fraction

When linear PDMS chains are crosslinked and converted into a network, i.e. using the hydrosilylation reaction, always a sol fraction has been found. The amount of sol fraction depends on the chosen starting materials and processing conditions and may be about 1% for optimum conditions [48].

Many researchers have reported adhesion hysteresis for crosslinked PDMS networks after the extraction of the sol fraction from these materials [26-29, 34-36]. Unfortunately, these experiments were done using somewhat different PDMS materials. Moreover, the PDMS network studied were, generally, not well characterized. This makes it difficult to compare these results. For instance, even when the starting materials are the same, differences in H/V ratios will lead to different network structures, such as difference in crosslink density, defects (unreacted groups and dangling chains) and amounts of sol fraction. Secondly, the crosslink density may change during the swelling and deswelling process. Last but not least, after the sol fraction is extracted, the surface morphology and roughness may also change. Any changes in these factors are expected to influence the measured adhesion hysteresis. Therefore, we studied the effect of extraction of sol fraction from the lenses and sheets on self-adhesion hysteresis in more detail. The sol fractions appeared to be relatively small (2 ~ 3%) (see Table 4.1). The results of the JKR measurements on these crosslinked PDMS networks after extraction are listed in Table 4.3. All JKR data shown were tested at a fixed loading-unloading motor speed (200 nm/s) with a waiting time of 5 s.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sol, wt %</th>
<th>$E_{\text{eff}}$, MPa</th>
<th>$W_{\text{eff}}$, mJ/m$^2$</th>
<th>$E_{\text{eff}}$, MPa</th>
<th>$W_{\text{eff}}$, mJ/m$^2$</th>
<th>$W_{\text{po}}$, mJ/m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>extracted PDMS 6</td>
<td>2.52</td>
<td>1.21</td>
<td>41.6</td>
<td>1.20</td>
<td>45.5</td>
<td>45.8</td>
</tr>
<tr>
<td>extracted PDMS 9</td>
<td>2.84</td>
<td>1.03</td>
<td>41.8</td>
<td>1.05</td>
<td>45.9</td>
<td>45.9</td>
</tr>
<tr>
<td>extracted PDMS 17</td>
<td>2.93</td>
<td>0.91</td>
<td>41.1</td>
<td>0.91</td>
<td>44.5</td>
<td>44.3</td>
</tr>
<tr>
<td>extracted PDMS 28</td>
<td>2.68</td>
<td>0.83</td>
<td>41.1</td>
<td>0.83</td>
<td>49.8</td>
<td>49.1</td>
</tr>
</tbody>
</table>

* measured at a motor speed of 200 nm/s, waiting time: 5 s.

Comparing the elastic moduli listed in Table 4.2 and Table 4.3, it was found that the extraction of the sol fraction did not influence the elastic moduli of the materials.
Also the $W_{ul}^{\text{eff}}$ and $W_{ij}^{\text{eff}}$ values obtained after extraction were equal to the values measured for PDMS 6, PDMS 9 and PDMS 17 before extraction (Table 4.2 and 4.3). The $G_{ul}^{\text{eff}} - G_{ij}^{\text{eff}}$ values were equal before and after extraction for these materials within the error of measurement and appeared to be constant for the waiting time of 15 min (Figure 4.5 and 4.6). In the previous chapter, the occurrence of adhesion hysteresis in these materials was explained by bulk viscoelastic losses. This is an energy dissipation mechanism not influenced by surface effects. As will be discussed in detail later on in this chapter, extraction minimizes the sol fraction on the surfaces of these materials. Hence, our findings discussed in this section for PDMS 6, PDMS 9 and PDMS 17 are in line with the proposed adhesion hysteresis mechanism in the previous section, namely bulk viscoelastic losses.

As mentioned in Chapter 2, all samples tested here were prepared with an optimum H/V ratio (H/V = 1.6), in order to obtain “perfect” networks which contained a minimum amount of defects in the crosslinked PDMS networks. When two surfaces of these “perfect” PDMS networks are brought into contact, only van de Waals interactions occur at the interface, thus no adhesion hysteresis is expected under equilibrium conditions, before and after extraction. However, this was not what we observed for PDMS 6, PDMS 9 and PDMS 17, because $W_{ij}^{\text{eff}}$ values were not equal to $W_{ul}^{\text{eff}}$ before and after extraction. We have attributed this hysteresis to the bulk viscoelastic losses, as discussed in the previous section. For PDMS 28 our findings are quite different, which will be discussed in more detail below.

We studied the effect of increasing waiting time up to 15 min on the $G_{ul}^{\text{eff}}$ values. The plot of $G^{\text{eff}}$ versus $a$ for PDMS 28 is also shown in Figure 4.6. The $G_{ul}^{\text{eff}}$ value changed with waiting time from $\sim 49 \text{ mJ/m}^2$ (waiting 5 s) to $\sim 57 \text{ mJ/m}^2$ (waiting 15 min). Comparing the $G_{ul}^{\text{eff}}$ values for PDMS 28 at a waiting time of 15 min before extraction (Figure 4.5) and after extraction (Figure 4.6), a higher $G_{ul}^{\text{eff}}$ value was found after extraction. No difference in $G_{ul}^{\text{eff}}$ values before and after extraction was found when a waiting time of 5 s was applied. Moreover, $G_{ul}^{\text{eff}} - G_{ij}^{\text{eff}}$ value observed
Self-adhesion study on crosslinked PDMS

for PDMS 28 was very similar to the ones observed for PDMS 6, PDMS 9 and PDMS 17. This suggests that when a waiting time of 5 s was used, the adhesion hysteresis in PDMS 28 is mainly caused by the bulk viscoelastic losses.

Several mechanisms can cause adhesion hysteresis in JKR measurements as was described in the introduction part. Recent literature show that the presence of impurities on the surface such as a linear and/or low molecular weight free PDMS chains can (partly) mask the adhesion hysteresis during the unloading of a JKR experiment [20, 36]. These impurities, often called sol fraction, can be (partly) extracted from the crosslinked PDMS materials with a solvent, which dissolves these chains. This swelling process may also disentangle chains; such chains may act as connector at the interface and contribute to hysteresis.

**Figure 4.6.** Plot of $G^{\text{eff}}$ versus $a$ with different waiting times for extracted crosslinked PDMS 6, PDMS 9, PDMS 17, and PDMS 28. Motor speed: 200 nm/s.
In the self-adhesion experiments of our crosslinked PDMS materials discussed here, no chemical bridging or hydrogen bonding is expected (see also in Chapter 4.5). As will be discussed later on, the swelling experiments do not change the roughness of the surfaces. Equal values of $E_{\text{eff}}$ and $E_{\text{ul}}^{\text{eff}}$ for crosslinked PDMS 28 were found before and after extraction. This strongly suggests that additional crosslinking and/or disentanglement of physical crosslinks in the bulk during extraction are minimal. Hence, the observed time-dependent hysteresis in PDMS 28 has to be explained at least partly by other factors such as the sol fraction differences and/or the presence of dangling chains across the surface of the materials acting as connectors.

It is known that the crosslinked PDMS elastomers release low molecular weight PDMS oligomers during contact under pressure with a substrate [49-51]. These oligomers are transferred to the substrate forming a hydrophobic surface. Free PDMS chains, especially the relatively shorter chains due to their higher mobility, tend to migrate to the interface of the two samples in contact. These chains may act as lubricants to prevent the occurrence of other possible mechanisms for hysteresis. We checked the presence of such sol fractions by conducting a simple experiment. Several clean Polystyrene (PS) and silicon wafer substrates were brought into contact with our non-extracted crosslinked PDMS sheets for 3 min, and a low pressure was applied to make an intimate contact. Contact angles with water were measured to see if the surface of the PS and silicon wafer were contaminated (with free PDMS chains migrated to the interface from the PDMS networks). The static contact angles of water were found to increase from 94° to 100° for PS substrates and 0° to 55° for silicon wafers, respectively. Hence, before extraction the surfaces of our PDMS lenses and sheets are contaminated by a sol fraction. In PDMS 28 an increase in adhesion hysteresis was observed after extraction. This suggests that in non-extracted PDMS 28 the sol fraction on the surface also has partially prevented hysteresis.

A conventional method to measure surface contamination is contact angle analysis. Dynamic contact angle measurements on our PDMS sheets were performed with water, which is a non-swelling liquid for PDMS. The dynamic contact angles with water were found to be different before and after extraction (Table 4.4). Before extraction, for all these samples an advancing ($\theta_a$) and a receding contact angle ($\theta_r$) of 106° and 101° was observed, respectively. After extraction, for all samples, the advancing contact angle increased to ~111°, and the receding contact angle decreased to ~91°. We found that the surface roughness did not change due to the extraction.
process (see also section 4.3.3). This strongly suggests that the chemical composition of the surfaces of these samples has been changed.

Another explanation may be the contamination of the solvent used during measurements. Uilk and co-workers [52] reported a lower $\theta_a$ and a higher $\theta_r$ for crosslinked PDMS coatings when they used contaminated water as the probing liquid. For crosslinked PDMS materials similar to our samples studied here, they found that before water contamination $\theta_a$ and $\theta_r$ were 116° and 97°, while after water contamination $\theta_a$ and $\theta_r$ were 108° and 104°, respectively. Their experimental evidence suggests that the water was contaminated by the siloxane species which diffused into the water droplet during the measurements. Those siloxane species are insoluble in water and of lower density than water, causing them to migrate to the water surface. According to these authors, extraction of cured PDMS samples would prevent this water contamination and allow measurement of the true contact angles. This conclusion was confirmed by a publication of Perutz et al. [34] for extracted crosslinked PDMS networks which reported 118° and 90° for the $\theta_a$ and $\theta_r$, respectively. Hence, our contact angle measurements strongly suggest that a sol fraction is always present before extraction in our crosslinked PDMS materials discussed here. After extraction, this sol fraction has been (largely) removed, which results in enhanced adhesion hysteresis for PDMS 28. We expect that this effect of sol fraction on hysteresis will be more remarkable when a larger amount of sol fraction is present in the materials (see Chapter 4.3.4 and 4.3.5).

Table 4.4. Contact angles with water of crosslinked PDMS samples before and after extraction.

<table>
<thead>
<tr>
<th></th>
<th>Before extraction</th>
<th></th>
<th>After extraction</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta_a$</td>
<td>$\theta_r$</td>
<td>$\theta_a$</td>
<td>$\theta_r$</td>
</tr>
<tr>
<td>PDMS 6</td>
<td>106.1±0.1</td>
<td>101.3±0.5</td>
<td>110.8±0.5</td>
<td>91.1±0.8</td>
</tr>
<tr>
<td>PDMS 9</td>
<td>106.4±0.2</td>
<td>101.6±0.3</td>
<td>111.4±0.4</td>
<td>92.0±0.8</td>
</tr>
<tr>
<td>PDMS 17</td>
<td>106.3±0.2</td>
<td>100.7±0.4</td>
<td>112.1±0.3</td>
<td>90.2±1.0</td>
</tr>
<tr>
<td>PDMS 28</td>
<td>105.8±0.2</td>
<td>102.0±0.5</td>
<td>109.7±0.5</td>
<td>90.7±0.7</td>
</tr>
</tbody>
</table>

It is often reported that after extraction the dangling and entangled PDMS chains cross the interface during the JKR experiments and enhance the adhesion hysteresis. With longer waiting times, the interpenetration of such chains is more effective. Indeed an increase in hysteresis with longer waiting times is observed in PDMS 28, which is in line with literature data.
Another reason for the observed increase in hysteresis for PDMS 28 may be the disentanglement of dangling and/or entangled chains during swelling. Physical entanglements are known to be present in crosslinked PDMS networks when the $M_n$ of the linear starting PDMS chain is higher than the molar mass for chain entanglement, $M_e (= 8100 \text{ g/mol})$ [53]. When swollen in a good solvent, some entangled and dangling chains may disentangle. During the JKR measurements these disentangled chains may further form connectors or physical bridges at the interface of the two samples. This chain disentanglement may also explain the higher and time-dependent adhesion hysteresis observed for PDMS 28 after extraction.

However, we should point out that the influence of the free chains and/or dangling chains on the adhesion hysteresis may be not as simple as indicated above. For example, the end groups of these chains may be polar because of conversion of Si-H into Si-OH by reaction with $\text{O}_2/\text{H}_2\text{O}$ [54-55]. Formation of hydrogen-bonding across the interface will complicate the interpretation of the observed hysteresis. Moreover, recent modelling on interface behaviour of connector chains indicates that reorientation of these chains and the number of connecting points may have a much larger influence than the length of the connector chain itself [22]. Also, the chain mobility is different for different chain length, which may influence the time-dependency of the measured hysteresis. Pickering [56] added 30% free long PDMS chains to the PDMS lens and tested the adhesion property between the PDMS lens and carboxyl terminated and $\text{CF}_3$-terminated thiol monolayer using the JKR technique. He observed a long “tail” in the contact radius versus force curve and attributed this to the formation of a capillary between the lens and the surface. These free long PDMS chains can migrate to the surface of the PDMS lens and act as connectors and form physical bridges across the interface. As we will show in Chapter 4.3.6, the effective average molecular weight between crosslinks of the crosslinked PDMS also has an important effect on adhesion hysteresis. Some of these factors will be discussed in more detail later on as well as their contribution to the adhesion hysteresis in PDMS 28.

Vaenkatesan et al. [57] used very similar PDMS materials to study the self-adhesion. They concluded that PDMS 28 did not show hysteresis. This may be (partially) explained by the fact that they used non-extracted materials and different measurement conditions, such as no waiting time.
4.3.3. Influence of surface roughness

The extraction of the sol fraction from an elastomeric network may change the surface roughness of the material. AFM was used to investigate the surface roughnesses of our samples before and after extraction on a nanometer scale. Examples of the height image of the PDMS 28 sheets after and before extraction are shown in Figure 4.7 and Figure 4.8, respectively. The root mean square roughness ($R_q$) data are summarized in Table 4.5. These results show that the surfaces of the tested PDMS sheets are quite smooth, and the surface roughness hardly changes after the sol fraction was extracted. This is understandable because of two reasons. Firstly, the amount of sol fraction in all PDMS samples tested here was small (< 3 wt %). Secondly, the de-swelling was conducted in such a way that methanol was added gradually to remove the solvent. Hence, because of the slow evaporation of the solvent, a sudden change in the surface morphology and the build up of defects (cracks and holes) on the surface was avoided. Based on above experimental results, we believe that the roughness of our PDMS samples does not play a role in the self-adhesion experiments discussed in Chapter 4.3.1 and 4.3.2.

Table 4.5. Root mean square roughnesses ($R_q$) of crosslinked PDMS sheets before and after extraction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_q$, nm, before extraction</th>
<th>$R_q$, nm, after extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS 9</td>
<td>0.96</td>
<td>0.94</td>
</tr>
<tr>
<td>PDMS 28</td>
<td>0.49</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Figure 4.7. AFM height image (a) and cross-section height diagram (b) of PDMS 28 sheet after extraction.
Figure 4.8. AFM height image (a) and cross-section height diagram (b) of PDMS 28 sheet before extraction.

Published data show that the surface roughness may increase after extraction when different crosslinked PDMS materials and/or de-swelling procedures are used. For instance, Choi and co-workers [26] reported an increase of $R_q$ from 2.8 nm to 11 nm after extraction. However, they concluded that the roughness increase observed by them did not influence the hysteresis, because their observed variation in surface roughness did not correspond to the observed variation in adhesion hysteresis.

Other literature [16, 26, 58] on self-adhesion of crosslinked PDMS materials also show that, roughness was not a key factor in influencing the hysteresis, because the surface roughness of PDMS was always quite low (within 10 nm), and crosslinked PDMS materials are very compliant which leads to a deformed contact area comparable to their original surface area.

4.3.4. Influence of dangling chains

Following the procedure proposed by Amouroux et al. [29], we prepared crosslinked PDMS materials with variable amounts of dangling chains by adding pentamethyldisiloxane (MM$^H$) to the reaction mixture. This small molecule has only one SiH group and will react with one vinyl end group of a PDMS chain to form a dangling chain on the network (provided the other chain end is linked to the network) (Scheme 4.2). However, adding MM$^H$ to the reaction mixture changes also the structure of the final network. The amount of free chains, dangling chains and the distance between crosslinks may increase when MM$^H$ is added before crosslinking. Indeed we found that the more MM$^H$ added, the larger the sol fraction and the lower elastic moduli (Table 4.6).
Table 4.6. Parameters of crosslinked PDMS samples with variable dangling chains.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\text{M}^\text{H}$/SiH $^b$</th>
<th>Sol fraction, wt %</th>
<th>$E_i^{\text{eff}}$, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS 6</td>
<td>0</td>
<td>2.52</td>
<td>1.18</td>
</tr>
<tr>
<td>PDMS 6-MM$^\text{H}$25</td>
<td>0.25</td>
<td>9.25</td>
<td>0.69</td>
</tr>
<tr>
<td>PDMS 6-MM$^\text{H}$33</td>
<td>0.33</td>
<td>15.40</td>
<td>0.56</td>
</tr>
<tr>
<td>PDMS 17</td>
<td>0</td>
<td>2.93</td>
<td>0.92</td>
</tr>
<tr>
<td>PDMS 17-MM$^\text{H}$25</td>
<td>0.25</td>
<td>8.31</td>
<td>0.26</td>
</tr>
</tbody>
</table>

$^a$ H/V = 1.6; $^b$ molar ratio of MM$^\text{H}$ to the total SiH groups.

The plot of $G_i^{\text{eff}}$ versus $a$ for the PDMS 6 and PDMS 17 series are shown in Figure 4.9a and 4.9b, respectively. All samples were tested at the same motor speed and waiting time. The $G_i^{\text{eff}}$ calculated with equation 1.1 did not depend on the amount of MM$^\text{H}$ added and are ~ 41.5 mJ/m$^2$, equal to the $G_i^{\text{eff}}$ and $W_i^{\text{eff}}$ values discussed in section 4.3.1 and 4.3.2. Apparently the measured $W_i^{\text{eff}}$ ($G_i^{\text{eff}}$) is independent of variations in the $M_n$ of the starting chains, sol fraction or amount of dangling chains under our measurement conditions. Based on $W_i^{\text{eff}}$ ($G_i^{\text{eff}}$) values, the calculated surface energy is ~ 20.8 mJ/m$^2$ according to equation 2.2. This corresponds to the surface energy of methyl groups on the surface [16].

Figure 4.9. $G_i^{\text{eff}}$ versus $a$ plot for non-extracted PDMS 6 (a) and PDMS 17 samples (b) made with different amounts of MM$^\text{H}$. Motor speed: 200 nm/s; Waiting time: 5 s.
The observed self-adhesion hysteresis was found to increase with increasing the amount of MM$_{H}$ added. As shown in Figure 4.9a and 4.9b, this increase was more obvious when larger amounts of dangling chains were present and a higher average molecular weight between crosslinks (or lower $E$ values, see Table 4.6) was obtained in PDMS 6 and PDMS 17 samples. PDMS 17-MM$_{H}^{25}$ showed a higher $G_{\text{eff}}^{\text{w}}$ than PDMS 6-MM$_{H}^{25}$ and PDMS 6-MM$_{H}^{33}$ under the same measuring conditions, indicating that not the amount of dangling chains but the length of the dangling chains are the dominating factor.

**Figure 4.10.** Plot of $G_{\text{eff}}$ versus $a$ for non-extracted PDMS 6-MM$_{H}^{33}$ for different waiting times. Motor speed: 200 nm/s.

**Figure 4.11.** Plot of $G_{\text{eff}}$ versus $a$ for non-extracted PDMS 17-MM$_{H}^{25}$ for different waiting times. Motor speed: 200 nm/s.
The influence of the variation in waiting time is shown in Figure 4.10 and 4.11 for PDMS 6-MM$^H$33 and PDMS 17-MM$^H$25, respectively. During unloading, the detachment begins when the energy release rate reaches a certain level. With longer waiting time, larger $G_{ul}^{\text{eff}}$ values and hysteresis were found.

![Figure 4.12](image.png)

**Figure 4.12.** Plot of $G_{l}^{\text{eff}}$ versus $a$ for PDMS 17-MM$^H$25 after extraction for different waiting times. Motor speed: 200 nm/s.

To check the influence of the sol fraction, we also tested the PDMS 17-MM$^H$25 sample after extraction with toluene. The plot of $G_{l}^{\text{eff}}$ versus $a$ is shown in Figure 4.12. The $G_{l}^{\text{eff}}$ value after extraction was equal to the $G_{l}^{\text{eff}}$ before extraction, however, the $G_{ul}^{\text{eff}}$ value and hysteresis changed considerably. After extraction, the adhesion hysteresis observed after waiting only 5 s was close to that of the non-extracted sample after waiting for 30 min. The $G_{ul}^{\text{eff}}$ value increased significantly with time, reaching about 100 mJ/m$^2$ after waiting for 5 min. The increase in self-adhesion hysteresis with time after extraction of our PDMS 17-MM$^H$25 can be explained in two ways. Firstly, after extraction the sol fraction at the surface is gone and no longer prevents any other possible causes of hysteresis. Another explanation is that by swelling entangled chains become less entangled and more easily form physical bridges at the interface in the limited time of contact between the lens and sheet.

Raphaël and de Gennes [38] have proposed a model based on an equilibrium contact...
configuration to explain the influence of connector chains on adhesion energy. In their model the adhesion energy arises from two sources: the thermodynamic work of adhesion $W$ and the suction work required to pull out the connectors. They proposed that a minimum number of surface density or a minimum length of the connectors is required to enhance significantly the adhesion energy. The threshold energy release rate at the tip, $G_0$, was predicted by:

$$G_0 - W \propto \gamma \Sigma N$$  \hspace{1cm} (4.2)

where $W$ is the thermodynamic work of adhesion, $\gamma$ is the surface energy of the bridging chains, $\Sigma$ is the areal density of the bridging chains, and $N$ is the polymerization index of the connector. According to equation 4.2, the adhesion hysteresis increases linearly with the amount and the length of connector chains present on the surface of the contacting materials [29, 59].

However, equation 4.2 is based on an equilibrium situation whereas our $G_{ul}^{eff}$ values are expected to be measured in a non-equilibrium state, as is generally met in practice [60]. The chosen contacting times in our experiments are far too short to reach an equilibrium condition and the observed hysteresis will be kinetically controlled. To reach an equilibrium condition for our measurements, a contact time of hours or even days are needed. Amouroux et al. [29] reported that a plateau of $G_{ul}^{eff}$ value of ~500 mJ/m$^2$ was observed after a waiting time of 1 day. They found this by studying the self-adhesion between two crosslinked PDMS samples which were made in a very similar way to our materials.

Léger et al. [59] reported that a contact time of longer than 1 month was needed to reach the equilibrium plateau of $G_{ul}^{eff}$ value by studying the adhesion between a crosslinked PDMS lens and a PDMS brush substrate. She found that the efficiency of the connector chains cannot be described by equation 4.2 because the kinetics of the interpenetration process is very slow. The $G_{ul}^{eff}$ value is only weakly affected by the length of the connector chains as long as the waiting time is relatively short. No information about the influence of the surface areal density of dangling chains during short contact time is given. She also indicated that the $G_{ul}^{eff}$ values in the transient stage appeared to be mainly governed by the distance between crosslinks of the
network.

The kinetics of interdigitation of chains across the interface has been analyzed theoretically by Connor and co-workers [61]. They suggested a two-step process. Firstly, the free end of the chain has to enter the other network at a point which may be far from its tethered end. Secondly, the chain has to find its equilibrium configuration in the network it entered. Both steps are facilitated strongly by the low \( T_g \) of our materials studied here.

When we compare the network structure of PDMS 6-MM\( ^{\text{H25}} \) with PDMS 17-MM\( ^{\text{H25}} \), it is clear that the dangling chain length of PDMS 17-MM\( ^{\text{H25}} \) are on average about three times the chain length of PDMS 6-MM\( ^{\text{H25}} \), whereas the number of dangling chains of the latter is three times that of the former one. According to equation 4.2, similar \( G_{\text{eff}} \) values would be expected for both materials. However, this has not been observed by us: the hysteresis of PDMS 17-MM\( ^{\text{H25}} \) is larger. This strongly suggests that equation 4.2 cannot be applied under measurement conditions used by us. We notice that the average molar mass between crosslinks \( (M_c) \) is much larger in PDMS 17-MM\( ^{\text{H25}} \) (see section 4.3.6). This suggests that the larger \( G_{\text{eff}} \) values found for non-extracted and extracted PDMS 17-MM\( ^{\text{H25}} \) may be mainly explained by the larger \( M_c \) values and not by the amount or length of dangling chains. This will be discussed in more detail in section 4.3.6.

The self-adhesion hysteresis is enhanced further by extracting the sol fraction from both materials before measurements. We have to point out that any chemical or hydrogen bond which might be formed across the interface during contact will promote adhesion too, and may dramatically increase the adhesion hysteresis. A recent model [22] using molecular dynamics simulations has been proposed to predict the contact time dependence on adhesion hysteresis of crosslinked PDMS networks on Si–OH surfaces. An important outcome of this simulation is that not the formation of more or stronger bonds is the main factor, but the redistribution of the beads on the polymer chains that form hydrogen bonds with the Si–OH surface is the more important factor. The importance of these contributions for our materials will be discussed in the following section and in Chapter 5.
4.3.5. Influence of excess of crosslinker used

All crosslinked PDMS materials discussed so far in this chapter were prepared using an H/V ratio of 1.6. These crosslinked PDMS materials are likely to have a minimum number of network defects as long as no dangling chains are introduced. When a larger amount of crosslinker is added to the reaction mixture, more dangling and unreacted Si–H groups are expected to be present in the network. The amount of free chains and average molecular weight between crosslinks may also increase with an increase in the H/V ratio above 1.6.

To study the effect of an excess of crosslinker on the self-adhesion of our samples, a detailed comparison was made between crosslinked PDMS 9 networks prepared with H/V = 1.6 and H/V = 2.5 before and after extraction. For some crosslinked samples, the activity of the Pt catalyst was poisoned by adding 1-dodecanethiol (~ 300 ppm) to the last swelling bath of toluene according to the procedure reported before [34]. The sol fractions, the elastic moduli ($E_i^{\text{eff}}$) of the PDMS 9 samples studied are listed in Table 4.7. The lowering of the $E_i^{\text{eff}}$ by ~ 30 % for PDMS 9 (H/V = 2.5) in relation to PDMS 9 (H/V = 1.6) suggests that the effective average molecular weight between crosslinks decreased by about 30 % (see also section 4.3.6).

All PDMS 9 (H/V = 1.6) samples of Table 4.7, as discussed in sections 4.3.1 and 4.3.2, showed a constant $G_i^{\text{eff}}$ and $G_{ul}^{\text{eff}}$ values of about 41 mJ/m$^2$ and 46 mJ/m$^2$, respectively, and these values did not change when a longer waiting time (15 min) was applied. As has been shown before, the difference between the value of $G_{ul}^{\text{eff}}$ and $G_i^{\text{eff}}$ is caused by bulk viscoelastic losses under our measurement conditions.

For PDMS 9 (H/V = 2.5) samples, the plots of $G^{\text{eff}}$ versus $a$ using different waiting times are shown in Figure 4.13. For the non-extracted PDMS 9 (H/V = 2.5) samples of Table 4.7, $G^{\text{eff}}$ values for both loading and unloading curves are very similar to PDMS 9 (H/V = 1.6), and no time-dependent $G_{ul}^{\text{eff}}$ values were found under our measurement conditions. However, after extraction, time-dependent $G_{ul}^{\text{eff}}$ values were
obtained. Poisoning the Pt catalyst slightly lowered these values for extracted samples.

Table 4.7. Some parameters of the crosslinked PDMS 9 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>sol, wt %</th>
<th>$E'_{\text{eff}}$, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS 9 (H/V=1.6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-extracted</td>
<td>-</td>
<td>1.01</td>
</tr>
<tr>
<td>Extracted</td>
<td>2.84</td>
<td>1.03</td>
</tr>
<tr>
<td>Extracted + poisoned</td>
<td>2.84</td>
<td>1.03</td>
</tr>
<tr>
<td>PDMS 9 (H/V=2.5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-extracted</td>
<td>-</td>
<td>0.81</td>
</tr>
<tr>
<td>Extracted</td>
<td>6.81</td>
<td>0.72</td>
</tr>
<tr>
<td>Extracted + poisoned</td>
<td>6.81</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Several explanations have been given for the adhesion hysteresis when an excess of crosslinker was used in the reaction mixture. One explanation is based on the conversion of the excess Si–H groups into Si–OH groups, forming hydrogen bonds across the interface when two samples are brought into contact under pressure [20, 34]. Several studies have shown that the Si–H groups can be thermally oxidized/hydrolyzed into Si–OH groups (reaction a, b) during and after the crosslinking reaction when air/water is present [55-56].

\[
\equiv\text{Si–H} + \frac{1}{2}\text{O}_2 \rightarrow \equiv\text{Si–OH} \quad \text{(a)}
\]

\[
\equiv\text{Si–H} + \text{H}_2\text{O} \rightarrow \equiv\text{Si–OH} + \text{H}_2 \quad \text{(b)}
\]
\[ \equiv \text{Si}-\text{OH} + \equiv \text{Si}-\text{H} \rightarrow \equiv \text{Si}-\text{O}-\text{Si} = + \text{H}_2 \]  
\[ \equiv \text{Si}-\text{OH} + \equiv \text{Si}-\text{OH} \rightarrow \equiv \text{Si}-\text{O}-\text{Si} = + \text{H}_2\text{O} \]

The oxidation/hydrolysis of the Si–H groups occurs more slowly than the hydrosilylation reaction and is only relevant when the Si–H groups are present in significant excess [55-56]. These converted Si–OH groups can react further with other Si–H and/or Si–OH groups (reaction c, d) leading to the formation of extra chemical crosslinks.

We tried to use FT-IR to check this possible conversion. However, no clear evidence of the formation of Si–OH groups was found. The stretching band located at 2136 cm\(^{-1}\) assigned to Si–H groups was always present after crosslinking, although with a much smaller intensity than the expected values based on the amount of excess Si–H used in the formulation (Figure 4.14). These spectra did not show large differences for samples before and after extraction and poisoning of the catalyst. Hence, our IR data suggest that most of the excess of Si–H groups react further and form additional crosslinks during preparation of our materials.

![Figure 4.14. FT-IR spectra of PDMS 9 samples with different H/V ratios after extraction.](image)

Some researchers reported that the adhesion hysteresis may originate from the complexation between the Si–H groups of the excess crosslinker and the hydrosilylation reaction between the unreacted Si–H groups and vinyl groups in the presence of an active Pt catalyst during the JKR experiments [20, 21, 36]. It was also shown that after poisoning of the catalyst the adhesion hysteresis dramatically reduced.
[21, 36]. Considering the fact that the band of (left-over) Si–H groups was observed in the spectra shown in Figure 4.14, a complexation between the left-over Si–H groups and the active Pt catalyst across the interface is possible in our materials. However, for the extracted PDMS 9 (H/V = 2.5) samples after poisoning the catalyst, the adhesion hysteresis was found to be only slightly lower than for the extracted samples without poisoning the catalyst, indicating that the contribution to hysteresis from this complexation, if any, was small for our samples.

Although a large variation in H/V ratios (1.0-2.5) were used to crosslink the linear PDMS 9 polymers, the influence on the elastic modulus is small (Table 2.2). This suggests that additional chemical crosslinks and physical crosslinks are formed in the bulk of the materials during the crosslinking reaction. This is confirmed by our FT-IR data. These data suggest that most of the unreacted Si–H groups were converted into Si–OH groups which reacted further according to reaction c and d mentioned above. Hence, it is unlikely that hydrogen bonding at the interface between the lens and sheet contributes considerably to the adhesion hysteresis of the extracted PDMS 9 samples.

Meanwhile, when the crosslinker is used in excess in the formulation, we cannot exclude that the amount of dangling chains and extended free chains has increased in the crosslinked network. These extended chains may stay permanently entangled because of the enlarged molecular weight and may not be removed by extraction. These chains could also act as connectors and promote adhesion.

4.3.6. Influence of the average molar mass between crosslinks ($M_c$)

As has been shown previously, adhesion hysteresis in our PDMS materials, which could not be attributed to bulk viscoelastic losses, was observed in PDMS 28, PDMS 6-MM$^{II}$ 25, PDMS 17-MM$^{II}$ 33, PDMS 17-MM$^{II}$ 25 and PDMS 9 (H/V = 2.5). The calculated $G_{ul}^{eff}$ values in these materials were dependent on the extraction of sol fraction and waiting time between the loading and unloading experiments. We also suggested that the $G_{ul}^{eff}$ values are dominated by the physical bridging of the connector chains at the interface and/or the variation in $M_c$ in these materials. Our results (section 4.3.4) indicated that the first explanation was not the main reason for hysteresis under the non-equilibrium states. The second explanation, however, is hardly mentioned in the literature as a source of adhesion hysteresis. Several rubber elasticity relations have been proposed to relate a rubber’s network
structure to its equilibrium mechanical properties. According to Graessley [62-63] and Flory [64-65] the elastic modulus for a perfect chemically crosslinked network, is given by

\[ E = 3\nu RT \]  
\[ E = 3(\nu - \mu)RT \]

for an affine and a phantom network, respectively. Here \( \nu \) is the concentration of active junctions, \( \mu \) the concentration of effective junctions, \( R \) the gas constant, and \( T \) the absolute temperature.

Langley [66] has proposed a small strain relation which includes the contribution of chain entanglements to the elasticity:

\[ E = 3(\nu - \mu)RT + 3T_e G_N^0 \]

where \( T_e \) is a trapping factor and \( G_N^0 \) is the plateau shear modulus which is between 0.2 and 0.3 MPa for PDMS [67]. The first term is the contribution of chemical crosslinking, given by the phantom network theory, and the second one is the contribution of the trapped entanglements of the polymer chains.

Another way to calculate the modulus \( E \) using the structure of a crosslinked network is [68]

\[ E = \frac{3\rho RT}{M_c} \]

where \( \rho \) is the density of the PDMS chain (~ 0.96 g/ml), \( M_c \) the average molar mass between chemical crosslinks when the physical entanglements are not present. When chain entanglements contribute to the elasticity, \( M_c \) is the average molar mass between crosslinks which include chemical and physical crosslinks. We assume that for these materials studied here both types of crosslinks can be present.

In principle this relation can be only applied well above \( T_g \), for an ideal network with a sufficient large and equal distance between the crosslinks. For the materials studied here the networks are not ideal, especially if dangling chains are present or an excess of crosslinker is used. The contribution chain entanglement to the elastic modulus is
Self-adhesion study on crosslinked PDMS

included in equation 4.5, but, unfortunately the data needed to calculate the elastic modulus according to equation 4.5 are not available for our materials. Hence, we focus on equation 4.6 to relate our measured $E_{l}^{\text{eff}}$ values to the network structure. Correction for loop and dangling chains are ignored, although it may affect the $E-M_c$ relation (eq. 4.6).

The measured $E_{l}^{\text{eff}}$ values and calculated $M_c$ values using equation 4.6 of our materials after extraction are listed in Table 4.8.

**Table 4.8.** Values of $E_{l}^{\text{eff}}$ and $M_c$ of crosslinked PDMS networks after extraction.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$M_n$</th>
<th>H/V</th>
<th>MM$^H$/SiH</th>
<th>Sol, wt %</th>
<th>$E_{l}^{\text{eff}}$, MPa</th>
<th>$M_c$, g/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS 6</td>
<td>6000</td>
<td>1.6</td>
<td>0</td>
<td>2.52</td>
<td>1.21</td>
<td>5700</td>
</tr>
<tr>
<td>PDMS 9</td>
<td>9400</td>
<td>1.6</td>
<td>0</td>
<td>2.84</td>
<td>1.03</td>
<td>6800</td>
</tr>
<tr>
<td>PDMS 17</td>
<td>17200</td>
<td>1.6</td>
<td>0</td>
<td>2.93</td>
<td>0.91</td>
<td>7800</td>
</tr>
<tr>
<td>PDMS 28</td>
<td>28000</td>
<td>1.6</td>
<td>0</td>
<td>2.68</td>
<td>0.83</td>
<td>8600</td>
</tr>
<tr>
<td>PDMS 6-MM$^H$33</td>
<td>6000</td>
<td>1.6</td>
<td>0.33</td>
<td>15.40</td>
<td>0.54</td>
<td>13300</td>
</tr>
<tr>
<td>PDMS 17-MM$^H$25</td>
<td>17200</td>
<td>1.6</td>
<td>0.23</td>
<td>8.31</td>
<td>0.23</td>
<td>31300</td>
</tr>
<tr>
<td>PDMS 9 (H/V=2.5)</td>
<td>9400</td>
<td>2.5</td>
<td>0</td>
<td>6.81</td>
<td>0.72</td>
<td>10090</td>
</tr>
</tbody>
</table>

The plot of average $G_{ul}^{\text{eff}}$ versus $E_{l}^{\text{eff}}$ value is shown in Figure 4.15. When the measured $E_{l}^{\text{eff}}$ value was smaller than ~ 0.9 MPa, self-adhesion hysteresis was observed before and after extraction, with a much higher hysteresis in the latter case. We have attributed this difference in hysteresis to the influence of a sol fraction present on the surface of the non-extracted materials (see section 4.3.2). The observed hysteresis appeared to be strongly dependent on the waiting time. The data in Figure 4.15 also strongly suggests that there is a direct relation between the calculated average $G_{ul}^{\text{eff}}$ and $E_{l}^{\text{eff}}$ for each material.
Because the amount of extracted sol fractions was not equal for the tested materials listed in Table 4.7, we focused on the samples after extraction to understand how the measured average $G_{ul}^{\text{eff}}$ values relate to the $M_c$ of the crosslinked materials. The results are shown in Figure 4.16. A threshold is clearly observed at the $M_c \sim 8000$ g/mol, very
close to the molar mass for chain entanglement, $M_e (= 8100 \text{ g/mol})$, for PDMS [53]. It is also interesting to observe that a reasonably linear relation exists between the average $G_{ul}^{\text{eff}}$ values and $1/M_c$ when $M_c$ is larger than this threshold.

Aforementioned observations suggest, at least under the measurement conditions used by us, the $G_{ul}^{\text{eff}}$ values are dominated by the average molar mass between crosslinks $M_c$ and not by the surface areal density and length of connector chains at the interface. This may be correct as was shown by Léger [59]. She concluded, for the contact between a PDMS lens and a solid surface with grafted PDMS chains, that the adhesion energy cannot be predicted by equation 4.2 before the equilibrium chain interpenetration is reached. She remarked that the kinetics of the interpenetration process of a connector chain is generally very slow, and appeared to be mainly governed by the molar mass between crosslinks and only weakly influenced by the length of the connector chains at relatively short contact times. Still an increase in the surface areal density of the grafted PDMS chains seems to enhance the adhesion hysteresis. However, no detailed information was given by her on the effect of surface areal density under short contact time.

Hence, our results suggest that, under our measurement conditions, the $M_c$ value seems to be the dominant factor in determining $G_{ul}^{\text{eff}}$ values. During the relative short contact time as we applied in our experiments, the surface chains can penetrate into the other side of the interface. The slow kinetics of this chain penetration process appeared to be governed by the $M_c$ values of both materials and to a much lesser extent by the amount and length of connector chains. As has been shown before chain entanglement may occur when $M_c$ is above 8100 g/mol. The facts that a small time-dependent $G_{ul}^{\text{eff}}$ was found for PDMS 28 ($M_c = 8600 \text{ g/mol}$) and that $G_{ul}^{\text{eff}}$ increased above $M_c \sim 8100 \text{ g/mol}$ with an increase in $M_c$, support this conclusion.

Chain entanglements across the interface can occur between chains which are actually connected to the network at both chain ends when the distance between the crosslinks are sufficiently long, and do not need to be dangling chains with only one chain end connected to the network. Any factors such as load/unloading rate, temperature, environmental gas, etc. which influence the kinetic process of interpenetration and entanglement of the chains will influence the calculated values of $G_{ul}^{\text{eff}}$. Therefore the
slope beyond the threshold (Figure 4.16) can be different when measurement conditions change.

As shown in Figure 4.15, the sample with the lowest the $E_i^{\text{eff}}$ value reached the highest average $G_{ul}^{\text{eff}}$ value of 123 mJ/m$^2$ for a waiting time of 15 min, which is comparable with literature data for similar materials [29, 44]. After a long contact time, equilibrium conditions are reached and a plateau of the $G_{ul}^{\text{eff}}$ value predicted by equation 4.2 will be reached. Published literature reported a $G_{ul}^{\text{eff}}$ value as high as ~500 mJ/m$^2$ [29, 59]. In such cases, the amount and the length of the connector chains seems to be the dominating factors for determining the $G_{ul}^{\text{eff}}$ value.

In practice often similar circumstances to our measuring conditions are met, i.e. the contact time is relatively short and a transient stage is met. Hence, our experimental results seem to offer a convenient way to predict, although not completely quantitively, the occurrence of adhesion hysteresis. The key factor is the threshold value for $M_c$ which can be taken conveniently as $M_e$. When the $M_c$ is larger than $M_e$, hysteresis is expected to increase (almost) linearly with $M_c$ and increase with contact time. The presence of sol fraction may (partially) mask the occurrence of adhesion hysteresis in crosslinked PDMS materials.

### 4.3.7. Influence of polar groups at the surface

Among the chemical origins for the adhesion hysteresis, hydrogen bonds across the interface may promote adhesion to a large extent, as reported in the literature [16, 20, 44, 68-69]. For instance, if silanol groups are present close to the surface of PDMS networks, the silanol groups prefer to remain below the surface because of the higher surface energy of Si–OH groups. When two such surfaces are brought into contact, a surface reconstruction may occur during contact, and the Si–OH groups can stretch to the interface and combine with the Si–OH and/or Si–O–O groups on the opposite surface to form hydrogen bonds or react with Si–OH to form $\equiv$Si–O–Si$\equiv$ bonds. A dramatic increase of adhesion hysteresis with contact time was observed between a crosslinked PDMS lens and SiO$_2$ surface by many researchers [39, 44, 68]. The measured hysteresis could be 1-2 orders of magnitude higher because of the reorganization of the network chains to form hydrogen bonds at the interface. A
significant isotope effect on adhesion hysteresis between a crosslinked PDMS lens and a silicon wafer was found when the Si–OH group was replaced by Si–OD [70]. The adhesion hysteresis increased dramatically for the Si–OD materials, which supports the mechanism of H–bonding with PDMS chains and also confirms that dissipative processes dominate adhesion behaviour.

For the self-adhesion of the materials discussed in this chapter, this effect hardly plays a role because of the lack of Si–OH groups. This aspect will be discussed in more detail in the next chapter where we discuss the adhesion properties of crosslinked PDMS materials containing in-situ precipitated SiO$_2$.

### 4.4. Conclusions

We investigated the influence of network structure, sol fraction, catalyst impurity and surface roughness on the self-adhesion behaviour of crosslinked PDMS materials using a newly built JKR apparatus. The values of $G_i^{\text{eff}}$ and $W_i^{\text{eff}}$ calculated from the loading part using the standard JKR model, were very stable for all materials tested and independent of variations in the $M_n$ of the starting chains, the the sol fraction, the amount and length of dangling chains present in the materials, under our measurement conditions. Hence, the $W_i^{\text{eff}}$ and $G_i^{\text{eff}}$ values obtained from the loading curve, when we neglect the small contribution of bulk viscoelastic losses, are the thermodynamic work of adhesion, which was equal for all materials studied in this chapter. This was confirmed by CA measurements. However, the behaviour as obtained from the unloading part is quite different.

The observed adhesion hysteresis for “perfect” crosslinked PDMS materials (PDMS 6, PDMS 9 and PDMS 17) measured at a motor speed of 200 nm/s and a waiting time of 5 s originates from the bulk viscoelastic loss, which can be diminished when a much lower motor speed is applied. No effect of $M_n$ on the adhesion hysteresis was found for these materials before and after extraction. Crosslinked PDMS 28 shows a small time-dependent hysteresis before and after extraction, when the waiting time between the loading and unloading part was well above 5 s.

The addition of MM$^H$ and/or an excess of crosslinker brought changes on the network structure and adhesion behaviour, showing a considerable increase in adhesion
hysteresis. The extraction of the sol fraction enhanced considerably the adhesion hysteresis. This may be explained by the absence of a sol fraction on the surface of the extracted materials which may (partially) mask the hysteresis.

For extracted materials, $M_c$ (or elastic modulus) can be used as a convenient parameter to predict the occurrence of adhesion hysteresis. When the $M_c$ value is larger than the threshold value $M_e \approx 8100$ g/mol, hysteresis increases almost linearly with $M_c$ and also increases with contact time. Under our measurement conditions, this increase may be explained by the interpenetration and entanglement of the surface chains which seems to be kinetically controlled by the $M_c$ values of both materials. The contribution of surface areal density and the length of dangling chains seem to be minor factors for hysteresis in our experiments.

The possibility of the formation of chemical bonds and/or hydrogen bonds across the interface as a source for the observed adhesion hysteresis was discussed. The effect of this factor for the materials studied here seems to be negligible. Also the roughness does not play a role in our case because the surfaces of our materials were very smooth before and after extraction.

References

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[67] (a) Valles, E.M, Macosko, C.M., Macromolecules 1978, 12, 673; (b) Langley, N.R., Ferry, J.D., Macromolecules 1968, 1, 353.


Chapter 5

Adhesion study on crosslinked PDMS containing in-situ precipitated SiO$_2$*

5.1. Introduction

Inorganic/organic hybrid materials prepared by the sol-gel method have received more and more attention in the past twenty years. The combination of organic and inorganic components gives these materials versatility in composition, structure and properties, which makes them very competitive and promising materials for applications in many fields such as optics, electronics, mechanics, sensors, and catalysis [1, 2].

As an important family of the hybrid materials, poly(dimethylsiloxane) (PDMS)-based hybrids are widely used as insulating materials, in medical devices, as membrane, in optical parts and antifouling and water-repellent coatings. Since in the early 1980’s Mark et al. [3-5] first “borrowed” the sol-gel method from the inorganic chemistry to prepare PDMS networks containing in-situ precipitated silica, this kind of inorganic/organic hybrid materials has been intensively studied on their preparation, [6-10] their mechanical properties [7-12], thermal stability [7,10-11], hydrophobicity [13-14] and transparency [15-17].

These PDMS-based materials are used as model hybrid networks for our study on the effect of inorganic fillers on the adhesion property of polymer coatings. Evidently, the surface and near surface composition, structures and morphologies are the dominating factors controlling their surface properties and adhesion behavior. However, in the literature, this field was seldom addressed and only very few studies [13, 18, 19] investigated these properties. Shindou et al. [13] studied the effects of heat-treatment temperature on the surface properties and surface morphologies of PDMS-based hybrid materials by using contact angle measurements and atomic force microscopy (AFM). They reported that the surface homogeneity changed before and after the heat-treatment at 300 °C. Martos et al. [18] used inverse gas chromatography to

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measure the surface energy of silica-TEOS-PDMS hybrids with 60 wt % inorganic component. They reported that the amount of PDMS was not enough to cover all silica surfaces, resulting in different surface energies of the surfaces originating from the presence of hydroxyl groups on silica surfaces. In contrast, Han et al. [19] added a small amount of PDMS to their system. They claimed that during the sol-gel process, the hydrophobic PDMS tended to be localized at the surface, thereby lowering the free energy of the system. These statements are incomprehensible and even contradictory at some points, making it very difficult to understand how the surface properties, such as adhesion, are controlled by the chemical and physical factors such as surface composition, structures and morphologies of these hybrids. To do so, it is necessary to have deeper and broader understanding of the surface science of these materials.

The adhesion properties of such filled PDMS networks were hardly investigated in the literature. Demir and co-workers [20] studied the effect of nanometer scale silica particles on the thermoelastic properties of filled PDMS networks. The silica particles were introduced into the polymer solution prior to crosslinking. However, no adhesion property was studied in their work. Oláh and co-workers [21] reported the work of adhesion and surface energy of slightly filled PDMS networks prepared from a commercial product package using their home-built JKR apparatus. The surface energy was found to be $\sim 21 \text{ mJ/m}^2$, but no further results, such as hysteresis, were reported in their work.

This chapter focuses on the study on the surfaces of PDMS-based inorganic/organic hybrid materials prepared by the sol-gel method. We investigated the bulk and surface composition, structure and morphology of the hybrids with different amounts of inorganic components. We used the JKR technique to study the adhesion properties of the surfaces of these hybrid materials made in contact with air and substrates, respectively.

### 5.2. Experimental

#### 5.2.1 Materials

Tetraethyl orthosilicate (TEOS), silanol-terminated poly(dimethylsiloxane) (PDMS) with a number-average molecular weight of 4200 (MWD = 1.82), vinyl-terminated PDMS with a number-average molecular weight of 6000 (MWD = 2.07), tetrakis(dimethylsiloxy)silane, dibutyltin diacetate and stannous 2-ethyl hexanoate
were purchased from ABCR, Germany. Cis-dichlorobis(diethyl sulfide)platinum(II) was obtained from Strem Chemicals. All materials were used without further purification.

5.2.2 Sample preparation
The hybrid samples were prepared via the sol-gel method. Silanol-terminated PDMS was mixed with TEOS with different molar feed ratios \( r = \frac{[\text{OEt}]}{[\text{OH}]} \), where the \(-\text{OC}_2\text{H}_5\) groups and the \(-\text{OH}\) groups are of the TEOS and PDMS, respectively (each TEOS molecule has four \(-\text{OEt}\) groups and each PDMS molecule has two \(-\text{OH}\) groups). After the solution was stirred for 10 min, two catalysts, dibutyltin diacetate and stannous 2-ethyl hexanoate, were added into the solution with concentrations of 1.0 wt% and 1.7 wt% of the PDMS, respectively. The mixture was stirred for another 10 min, degassed and cast into a polystyrene (PS) petri-dish to gel at room temperature in air for 48 h and then at 50 °C under vacuum (~ 0.01 mbar) for another 24 h. Some samples were also cast onto silicon wafers and Al substrates using the same preparation method. The sample surfaces exposed to air were named as A-* and sample surfaces contacting PS, Al and Si wafer as PS-*, Al-* and Si-*, respectively. For example, A-r30 represents a sample prepared with the molar feed ratio \( r \) of 30 and the surface studied is the one exposed to air. No water was added to the reaction mixtures except as was absorbed by the samples from the humidity in the air [4, 17]. All samples were ca. 1 mm thick, transparent, rubbery and could be easily peeled off from the substrates. These samples were characterized and tested as prepared without extraction with solvent.

A reference sample exposed to air, denoted as Ref-PDMS, was prepared by cross-linking vinyl-terminated PDMS and tetrakis(dimethylsiloxy)silane with cis-dichlorobis(diethyl sulfide)platinum(II) as the catalyst, as shown in Chapter 2 Scheme 1. The mixture was cast into a polystyrene petri-dish and cure at 60 °C for 3 days under vacuum (~ 0.01 mbar). This non-extracted sample is used as reference sample (0% SiO\(_2\)), because it is cross-linked through hydrosilylation reaction, thus a pure soft PDMS network is formed.

5.2.3 Methods
The densities of the samples were determined by pycnometry. The weight concentrations of SiO\(_2\) are calculated from density data using values of \( d = 0.96 \text{ g/cm}^3 \) for PDMS networks and \( d = 2.2 \text{ g/cm}^3 \) for silica [22]. The reduced moduli (\( E_i \)) near
the surface (~ 10 µm) of the samples were measured in air at room temperature using micro-indentation with a Berkovich indenter following a procedure described elsewhere [23-24].

Attenuated total reflectance-infrared (ATR-IR) spectroscopy was performed using a BIORAD Excalibur Spectrometer at room temperature. All spectra were recorded under dry N\textsubscript{2} at room temperature between 4000 and 650 cm\textsuperscript{-1} with a resolution of 2 cm\textsuperscript{-1} co-adding 30 scans. All spectra were normalized by the C-H bending band of the PDMS backbone located at 1259 cm\textsuperscript{-1}.

The cross-sectional morphologies of the samples were investigated using a Philips environmental scanning electron microscope XL-30 ESEM REG (Philips, now FEI Co., Eindhoven). Imaging of the sample cross-section on a fracture surface was performed in high-vacuum mode using acceleration voltages of 1 kV (low-voltage SEM, LVSEM) and a secondary electron (SE) detector.

Nanoscale morphological surface properties were measured by using atomic force microscopy (AFM) (NTEGRA, NT-MDT, Moscow). The topography and phase images were obtained in the intermittent contact mode with Si-cantilevers, spring constant k = 5.5 N/m (NSG01, NT-MDT, Moscow). A sample area of 1 × 1 µm was scanned. The measurements were performed in air at room temperature at a humidity of 45 ~ 50%.

X-ray photo-electron spectroscopy (XPS) was conducted with a VG Escalab 200 using a standard aluminum anode (Al-K\textalpha\textsubscript{1}486.3 eV) operating at 510 W. Spectra were recorded at room temperature at normal emission at background pressure of 5 × 10\textsuperscript{-10} mbar, at take-off angles of 15, 30 and 90° with respect to the plane of the sample. All binding energies were referenced to the C 1s peak at 284.6 eV [25].

Low-energy ion scattering (LEIS) experiments were performed under vacuum at room temperature with the Calipso instrument operated with a 3 keV \textsuperscript{3}He\textsuperscript{+} ion beam that is most sensitive for low atomic number elements. The measurements were performed on specimen areas of 2 × 2 mm\textsuperscript{2}. The total ion dose used was of the order of 5 × 10\textsuperscript{13} ions/cm\textsuperscript{2}.

Dynamic contact angles (DCA) analysis was performed in air at room temperature using the sessile drop method with an apparatus OCA30 (Dataphysics Instruments).
Distilled water was used as the probe liquid. All advancing and receding contact angles given are the average value of at least five measurements on different positions of the sample.

JKR experiments were conducted, on the surfaces of hybrid samples made according to the procedure introduced in Chapter 2. PDMS hemispheres (PDMS 9) were used as the probing lenses and the hybrid samples were tested as the sheet samples. PMDS 9 lenses were prepared with an H/V ratio of 1.6 according to the procedure mentioned in Chapter 2.2.2. The elastic moduli of these lenses were measured to be 1.01 MPa (see Table 2.4). A loading/unloading speed of 200 nm/s was used in all experiments conducted in this chapter. A waiting time of 5 s was always used in all experiments unless mentioned otherwise.

5.3. Results and discussion

5.3.1 Material preparation

\[
\text{Hydrolysis:} \quad \text{Si}(\text{OEt})_4 + 4\text{H}_2\text{O} \xrightarrow{\text{Cat.}} \text{Si(OH)}_4 + 4\text{EtOH}
\]

\[
\text{Condensation:}
\]

\[\text{Self-condensation} \quad \text{O-Si-OH} + \text{HO-Si-O} \xrightarrow{\text{Cat.}} \text{O-Si-O-Si-O} + \text{H}_2\text{O}\]

\[\text{Co-condensation} \quad \text{O-Si-OH} + \text{HO-} (\text{Si-O})_n \xrightarrow{\text{Cat.}} \text{O-Si-O-Si-O} + \text{H}_2\text{O} \quad (n \geq m)\]

Scheme 5.1

The synthesis of our hybrid materials by the sol-gel method involves the basic steps as shown in Scheme 5.1: hydrolysis of TEOS, the self-condensation of the –OH groups of hydrolyzed TEOS, the self-condensation of the –OH groups of silanol-terminated PDMS, and the co-condensation between the –OH groups of hydrolyzed TEOS and
the –OH groups of silanol-terminated PDMS. As the self-condensation is going on, SiO\(_2\) is precipitated in situ and thus a hybrid material is formed. The co-condensation between the –OH groups of PDMS and hydrolyzed TEOS results in chemical bonds between the SiO\(_2\) and PDMS phase [4, 26].

The sol-gel process was studied by ATR-IR spectroscopy. The disappearance of the –OEt group of TEOS was followed by measuring the change in the Si–OEt stretching bands (1167, 1072 and 957 cm\(^{-1}\)) [27] and the C–H stretching bands of the ethyl groups (2976, 2930 and 2890 cm\(^{-1}\)). The C–H bending bands of ethyl groups of TEOS are located in the range of 1350-1480 cm\(^{-1}\). The spectra of r30 mixture at different curing time are presented in Fig 5.1a. All these bands decrease during cure, as expected, and are no longer visible after cure, showing that the hydrolysis of –OEt groups of TEOS is (almost) complete after cure.

![ATR-IR spectra](image)

**Figure 5.1a.** ATR-IR spectra of the r30 sample for curing time of (a) 0 min; (b) 18 min; (c) 38 min; (d) 68 min and (e) 148 min.

To check if A-* and Si-* surfaces show any difference in the probing depth of ATR-IR (\(\sim 1 \mu m\)), we collected the spectra of A-* and Si-* surfaces of cured samples for different \(r\) ratios. No measurable difference between the spectra of A-* and Si-* surfaces were observed, indicating that such a probing depth was too thick to reveal the difference, if there is, between the A-* and Si-* surfaces.
Adhesion study on crosslinked PDMS containing in-situ precipitated SiO₂

Fig 5.1b shows the ATR-IR spectra of the samples made using different r values after cure for 3 days. It is known from literature that precipitated SiO₂ has a strong band at 1080 cm⁻¹ and a very broad shoulder at about 1220 cm⁻¹ [27]. As is shown in this figure, an increase in these two bands indicates that when higher amounts of TEOS are present in the formulation, more SiO₂ is precipitated, in line with literature [4, 6]. A weak broad absorption band at around 3400 cm⁻¹ assigned to OH stretching was observed. This band can originate from water molecules or hydro-bonded Si–OH groups [28]. A very weak band centered at 1630 cm⁻¹ assigned to the bending of the water molecules showed the presence of a trace of water [29]. However, this band is fairly constant for all samples, indicating that the increase in the band at around 3400 cm⁻¹, observed when the r values are increased, originates from the increase of Si–OH groups. This agrees with literature that polar –OH groups are present at the surfaces of SiO₂ [30-32].

The cross-sectional morphologies of the samples were investigated by LVSEM. An example of r30 sample is shown in Fig. 5.2. The homogeneously dispersed SiO₂ particles have a size of about 50-200 nm. There are some SiO₂ aggregates (~ 1 µm) present in the samples.
Figure 5.2. LVSEM image of the cross-section of sample r30.

The increase in the amount of precipitated SiO$_2$ with increasing molar feed ratio $r$ was confirmed by density measurements on the cured samples (Table 5.1). Larger density value was obtained for a larger $r$ ratio. Using the difference in density between PDMS phase and precipitated SiO$_2$ phase, the bulk weight concentrations of SiO$_2$ of all samples were determined. A gradual increase in concentration with increasing $r$ was observed, which is in agreement with our ATR-IR results reported above. The elastic moduli of samples measured with micro-indentation, denoted as $E_{id}$, are listed also in Table 5.1. The increase with $r$ is in line with our knowledge on the reinforcement effects of inorganic fillers on a rubbery polymer material [4, 6, 26].

<table>
<thead>
<tr>
<th>$r^a$</th>
<th>Density, g/cm$^3$</th>
<th>SiO$_2$ wt%</th>
<th>$E_{id}^b$, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref-PDMS</td>
<td>0.959</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>1.2</td>
<td>0.969</td>
<td>0.80</td>
<td>1.0</td>
</tr>
<tr>
<td>2.5</td>
<td>0.986</td>
<td>2.18</td>
<td>1.9</td>
</tr>
<tr>
<td>6</td>
<td>1.001</td>
<td>3.39</td>
<td>3.9</td>
</tr>
<tr>
<td>10</td>
<td>1.014</td>
<td>4.44</td>
<td>4.4</td>
</tr>
<tr>
<td>20</td>
<td>1.040</td>
<td>6.54</td>
<td>6.0</td>
</tr>
<tr>
<td>30</td>
<td>1.066</td>
<td>8.64</td>
<td>9.6</td>
</tr>
<tr>
<td>50</td>
<td>1.137</td>
<td>14.30</td>
<td>20.7</td>
</tr>
</tbody>
</table>

$^a$ molar feed ratio $r = [\text{OEt}] / [\text{OH}]$.

$^b$ measured by micro-indentation and calculated by assuming Poisson’s ratio to be 0.5.

5.3.2 Surface properties of the hybrid materials

The adhesion between two materials is influenced strongly by the chemical
composition and morphology at the surfaces of the materials. In order to study the morphologies and chemical composition of these surfaces in more detail, a combination of AFM, XPS, LEIS and DCA analyses were used to investigate the surface properties.

The morphologies at a nanometer level of the sample surfaces were studied by using AFM, as shown in Fig. 5.3. The averaged roughness of several surfaces is listed in Table 5.2. The surfaces of sample A-r50 and Si-r50 have a similar averaged roughness of 2-4 nm, indicating a very smooth surface and no dependency of the roughness of the samples on the amount of SiO$_2$ present in the materials was found. The surfaces of sample Al-r50 and PS-r50 have a higher roughness. This difference originates from the roughness of the Al and PS substrates themselves, because the patterns shown are those of an Al and PS substrate.

![AFM topography mapping images](image)

**Figure 5.3.** AFM topography mapping images of (a) A-r1.2; (b) A-r10; (c) A-r30; (d) A-r50; (e) Si-r50; (f) Al-r50 and (g) PS-r50.
Table 5.2. Data of AFM and LEIS measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>AFM $R_a$ nm</th>
<th>LEIS Peak area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref-PDMS</td>
<td>3.6</td>
<td>25 17 58</td>
</tr>
<tr>
<td>A-r1.2</td>
<td>2.1</td>
<td>25 17 58</td>
</tr>
<tr>
<td>A-r10</td>
<td>2.4</td>
<td>-</td>
</tr>
<tr>
<td>A-r30</td>
<td>2.9</td>
<td>-</td>
</tr>
<tr>
<td>A-r50</td>
<td>3.1</td>
<td>25 17 58</td>
</tr>
<tr>
<td>Si-r50</td>
<td>2.6</td>
<td>27 15 58</td>
</tr>
<tr>
<td>Al-r50</td>
<td>7.8</td>
<td>27 16 57</td>
</tr>
<tr>
<td>PS-r50</td>
<td>10.5</td>
<td>27 15 58</td>
</tr>
</tbody>
</table>

* Averaged roughness

XPS was used to determine the atomic composition of the outmost 10 nm of the sample surfaces. Measurements were performed at take off angles of 90, 30 and 15°, giving estimated depths of penetration of about 10, 5 and 2 nm, respectively. For all samples, the binding energy for C$_{1s}$, O$_{1s}$ and Si$_{2p}$ were observed at 284.6, 532.1 and 102.1 eV, respectively. The silicon-to-oxygen configuration has a particular Si$_{2p}$ binding energy that is dependent on the number of oxygen atoms bonded to a silicon atom. The Si$_{2p}$ binding energy shifts to a higher value when more oxygen atoms are bonded to the silicon atom. The Si$_{2p}$ peak at 102.1 eV is assigned to an organic silicone phase and the peak at 103.8 eV is assigned to Si atoms bonded to three or four oxygen (SiO$_x$, $x = 3$, 4) [23, 33]. For sample surfaces in contact with air (A-r1.2, A-r30 and A-r50), the amount of C decreases and O increases with an increase in molar feed ratio $r$, indicating that more SiO$_2$ is precipitated in the top layer of 10 nm when a higher $r$ value is applied in the formulation (Table 5.3). This is confirmed by the increase of the Si$_{2p}$ peak area at 103.8 eV in respect to the peak area at 102.1 eV with increasing $r$. It deserves to be noticed that for the A-r1.2 and Si-r1.2 samples, no peak for the silica-like phase is found, showing that in the ~10 nm top layer, no silica is present. When the penetration depth is ~ 5 nm, some silica was still found for the A-r30 and A-r50 samples, but the amount was less than the value calculated over a depth of 10 nm. No silica was found in these samples at the top layer of ~ 2 nm. These results clearly show that for the surfaces made in contact with air, only PDMS is present at the 2 nm top layer of these surfaces. The amount of SiO$_2$ increases gradually from this top layer, however, even at 10 nm depth, the amount of SiO$_2$ is
Adhesion study on crosslinked PDMS containing in-situ precipitated SiO\textsubscript{2} less than that in the bulk of the samples.

Table 5.3. Results of XPS measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>Take off angle, °</th>
<th>Atomic composition % *</th>
<th>Peak area %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>Ref-PDMS</td>
<td>90</td>
<td>49</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>A-r1.2</td>
<td>90</td>
<td>49</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Si-r1.2</td>
<td>90</td>
<td>49</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>A-r30</td>
<td>90</td>
<td>47</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>2</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>A-r50</td>
<td>90</td>
<td>45</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Si-r50</td>
<td>90</td>
<td>39</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>22</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>Al-r50</td>
<td>90</td>
<td>41</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>18</td>
<td>82</td>
</tr>
<tr>
<td>PS-r50</td>
<td>90</td>
<td>42</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>18</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>15</td>
<td>85</td>
</tr>
</tbody>
</table>

* Calculated from atomic sensitivity factors for X-ray sources [34].

For the sample surfaces made in contact with substrates, the atomic composition is different from the surfaces made in contact with air. As listed in Table 5.3, Si-r50, Al-r50 and PS-r50 samples contain less carbon and more oxygen atoms. Putting aside the difference between the calculated atomic ratio for PDMS (C: O: Si = 50: 25: 25) and our measured value for Ref-PDMS (C: O: Si = 49: 31: 20), the atomic compositions of these three samples, compared to A-r50, are more close to the bulk value (C: O: Si = 37: 36: 27) calculated from weight fraction of SiO\textsubscript{2}. A comparison of the Si 2p binding energy of sample A-r50 (a, b, c) and Si-r50 (d, e, f) is shown in
Fig 5.4. The \( \text{Si}_{2p} \) peak area at 103.8 eV assigned to the inorganic silica-like phase is still present in the Si-r50 sample even when a penetration depth of \( \sim 2 \text{ nm} \) is applied. The variation found in \( \text{Si}_{2p} \) areas at 103.8 eV at different penetration depth is within the fault of measurement (\( \sim 5\% \)), suggesting that for the sample surfaces made in contact with substrates, the distribution of SiO\(_2\) phase is homogeneous from bulk to the top surface (\( \sim 2 \text{ nm} \)).

![XPS spectra of A-r50 at take off angles of (a) 90°; (b) 30° and (c) 15° and Si-r50 at (d) 90°; (e) 30° and (f) 15°. The Si 2p peak is resolved into the organic silicone 102.1 eV peak and the inorganic silica-like 103.8 eV peak.](image)

**Figure 5.4.** XPS spectra of A-r50 at take off angles of (a) 90°; (b) 30° and (c) 15° and Si-r50 at (d) 90°; (e) 30° and (f) 15°. The Si 2p peak is resolved into the organic silicone 102.1 eV peak and the inorganic silica-like 103.8 eV peak.

DCA analysis and LEIS were performed to investigate the properties of the outermost surface layer. It is known that the contact angle depends on both the chemical
composition of the surface and the surface roughness on the micrometer level [35]. The averaged roughness data (Table 5.2) show that all the tested surfaces are smooth with a roughness lower than ~10 nm, therefore we assume that any change of contact angles results from the chemical composition change. The contact angles with water of samples made in contact with air and substrates, for different molar feed ratio \( r \), are listed in Table 5.4. The advancing contact angles of surfaces in contact with air (A-r1.2, A-r10, A-r30 and A-r50) are constant at \(~105^\circ\) close to the values of 106.6° measured for Ref-PDMS. Hysteresis is also stable. This is in agreement with our previous XPS finding that these surfaces have a silica-free thin top layer of PDMS. For the surfaces in contact with substrates, the advancing contact angles decrease with increasing \( r \), to ~92° when \( r \) is 50. At the same time, hysteresis increases with increasing \( r \). There are two possibilities that can cause this change of contact angles. Some hydrophilic SiO\(_2\) exist at the surfaces and/or the SiO\(_2\) phases are located just beneath the outermost atomic layer. It is unlikely that SiO\(_2\) are located at the outermost layer because of its high surface energy and the flexibility of the PDMS chains, thus we assume that the SiO\(_2\) phases are beneath the outermost atomic layer. When the surface contacts with water, the –OH groups at the surface of SiO\(_2\) may extend towards the interface of water and the hybrid sample, making the sample surface less hydrophobic. To prove the above assumptions, we did LEIS experiments to study the chemical composition of the outermost atomic layer. The peak areas % of C, O and Si of different samples (Table 5.2) show very small differences. This seems to prove the above assumptions. Unfortunately, we cannot exclude that the error of measurements of LEIS is too large for observing these differences. Moreover, LEIS measurements were done under vacuum without the presence of moisture that may have enhanced the formation of a silica-free outermost atomic layer during our LEIS experiments.

Based on above studies, we propose two different surface structures for hybrid surfaces made in contact with air and with substrates, respectively. For the surfaces made in contact with air, there is at least a ~2 nm thick silica-free layer of PDMS at the surface, giving a surface property similar to the pure PDMS. For the surfaces made in contact with substrates, the precipitation of SiO\(_2\) is likely to occur directly at the interfaces, giving a surface property different from PDMS. The reasons for this difference in the presence of SiO\(_2\) at the surface might be complex. We believe that surface energies of PDMS, SiO\(_2\), and substrates do play an important role, but other factors such as the difference in the amount of water present on the substrates may be important too. After the samples are peeled off from the substrates, it seems to be
more likely that because of the flexibility of PDMS chains, migration of PDMS chains to the outermost atomic layer may occur [36, 37], by which polar –OH groups present at the surface of SiO$_2$ are covered with a PDMS layer. When these surfaces meet water, as happens in the DCA experiments, these –OH groups can easily stretch out to the surface, resulting in lower contact angles. Below the effect of these two different structures of these surfaces on adhesion properties will be discussed.

**Table 5.4.** Dynamic contact angles of A-, Si-, Al- and PS- samples with different molar feed ratio $r$ ($r = 1.2, 10, 30, 50$)

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\theta_{\text{adv}},^\circ$</th>
<th>$\theta_{\text{rec}},^\circ$</th>
<th>Hysteresis, $^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref-PDMS</td>
<td>106.6</td>
<td>101.9</td>
<td>4.7</td>
</tr>
<tr>
<td>A-r1.2</td>
<td>105.3</td>
<td>100.3</td>
<td>5.0</td>
</tr>
<tr>
<td>Si-r1.2</td>
<td>104.2</td>
<td>99.2</td>
<td>5.0</td>
</tr>
<tr>
<td>Al-r1.2</td>
<td>105.6</td>
<td>100.7</td>
<td>4.9</td>
</tr>
<tr>
<td>PS-r1.2</td>
<td>105.4</td>
<td>100.5</td>
<td>4.9</td>
</tr>
<tr>
<td>A-r10</td>
<td>105.4</td>
<td>100.6</td>
<td>4.8</td>
</tr>
<tr>
<td>Si-r10</td>
<td>95.3</td>
<td>89.5</td>
<td>5.8</td>
</tr>
<tr>
<td>Al-r10</td>
<td>97.8</td>
<td>92.7</td>
<td>5.1</td>
</tr>
<tr>
<td>PS-r10</td>
<td>97.9</td>
<td>92.9</td>
<td>5.0</td>
</tr>
<tr>
<td>A-r30</td>
<td>105.1</td>
<td>99.7</td>
<td>5.4</td>
</tr>
<tr>
<td>Si-r30</td>
<td>93.6</td>
<td>84.8</td>
<td>8.8</td>
</tr>
<tr>
<td>Al-r30</td>
<td>94.0</td>
<td>86.0</td>
<td>8.0</td>
</tr>
<tr>
<td>PS-r30</td>
<td>94.3</td>
<td>85.4</td>
<td>8.9</td>
</tr>
<tr>
<td>A-r50</td>
<td>104.7</td>
<td>99.4</td>
<td>5.3</td>
</tr>
<tr>
<td>Si-r50</td>
<td>91.3</td>
<td>81.4</td>
<td>9.9</td>
</tr>
<tr>
<td>Al-r50</td>
<td>92.4</td>
<td>81.7</td>
<td>10.7</td>
</tr>
<tr>
<td>PS-r50</td>
<td>92.9</td>
<td>83.1</td>
<td>9.8</td>
</tr>
</tbody>
</table>

**5.3.3. Adhesion properties**

In the previous sections of this chapter we have shown the surface morphology, structures and properties of the PDMS/SiO$_2$ hybrid materials. Our focus was given on the difference in the surfaces made in contact with air and substrates. It is reasonable to expect that such differences will influence the adhesion property of these surfaces because of the possible formation of hydrogen bonding. Therefore, we investigated the adhesion between a PDMS 9 lens and these surfaces using our newly built JKR apparatus.
5.3.3.1 Contact images
All experiments were conducted using a PDMS lens (PDMS 9) and a sample surface. Because all samples tested were optically transparent, we expected good contact images between the PDMS lens and the sample surfaces we studied previously. However, the contact images showed differences for the surfaces made in contact with air and different substrates. Examples of the contact images of the PDMS 9 lens and r50 samples are shown in Figure 5.5. For A-r50 and Si-r50 samples, the contact images were as good as the contact between two PDMS samples. The edge of the contact area of PS-r50 sample was a bit less smooth, whereas the contact image of Al-r50 sample was strongly interfered with the roughness features of the sheet. These features resulted from the roughness of the aluminium substrate. These imperfections will result in inaccuracy for the measurement of the contact radius \( a \), therefore only A- and Si- samples were studied in detail.

![Figure 5.5. Images of the contact between a PDMS lens (PDMS 9) and hybrid samples made in contact with air and different substrates (r = 50).](image)

5.3.3.2 Loading curves of JKR experiments
For the loading curves of our JKR experiments, the effective values of work of adhesion, \( W_i^{\text{eff}} \), and elastic constant, \( K_i^{\text{eff}} \), were obtained by fitting the loading curve according to the JKR equation (equation 1.4). The elastic moduli, \( E_i \), were further calculated based on the \( K_i^{\text{eff}} \) values. In the next section, we will discuss the variation.
in the elastic modulus and $W_i^{\text{eff}}$ of A- and Si- surfaces, respectively.

**The elastic modulus**

The elastic moduli measured using micro-indentation gave equal values for A- and Si-surfaces. The moduli obtained from our JKR loading experiments also showed no difference on A- and Si-surfaces within the error of measurements. The elastic modulus values measured using these two methods (Table 5.5) are in line with each other. This strongly suggest that the difference in the top layer for A- and Si-surfaces has no influence on the measured modulus values, for both micro-indentation and JKR techniques.

**Table 5.5. Comparison of the elastic modulus values measured by JKR and micro-indentation**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_i^{\text{eff}}$, MPa</th>
<th>$E_{\text{id}}$, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-r 1.2</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Si-r 1.2</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>A-r10</td>
<td>4.9</td>
<td>4.4</td>
</tr>
<tr>
<td>Si-r10</td>
<td>5.0</td>
<td>4.8</td>
</tr>
<tr>
<td>A-r30</td>
<td>7.6</td>
<td>9.6</td>
</tr>
<tr>
<td>Si-r30</td>
<td>7.7</td>
<td>9.5</td>
</tr>
<tr>
<td>A-r50</td>
<td>19.3</td>
<td>20.7</td>
</tr>
<tr>
<td>Si-r50</td>
<td>19.5</td>
<td>21.0</td>
</tr>
</tbody>
</table>

$^a$ measured by JKR and calculated from $K_i^{\text{eff}}$ by assuming the Poisson’s ratio to be 0.5.

$^b$ measured by micro-indentation and calculated by assuming Poisson’s ratio to be 0.5 (see Chapter 3).

Several publications reported the calculation of the elastic modulus based on JKR results [38-42]. Wahl et al. [41] compared the modulus values calculated from indentation (Berkovich indenter) and JKR curve fitting in a recent publication. Their results showed that the modulus values calculated from these two methods were in agreement with each other. These publications confirmed our findings. Moreover, our data in Table 5.5 proved the reliability of measuring the elastic modulus using the JKR technique, for materials with much larger elastic modulus than crosslinked PDMS itself. Furthermore, we calculated the modulus values by fitting the $a^3$-$P$ curve and did not use the indentation displacement (see Figure 2.9) which is often applied in
the literature. The discussion of the application of indentation displacement in the calculation of the elastic modulus is outside of the scope of this thesis.

**The values of \( W_i^{\text{eff}} \)**

By fitting the loading part of the \( a^3-P \) curve, we also obtained the work of adhesion (\( W_i^{\text{eff}} \)) for A- and Si- samples prepared with different \( r \) ratio. These \( W_i^{\text{eff}} \) values, together with the surface energies (\( \gamma_{\text{CA}} \)) of these surfaces measured from contact angle analysis, are listed in Table 5.6. Both the \( \gamma_{\text{CA}} \) and \( W_i^{\text{eff}} \) values for the A- surfaces were equal to the values for PDMS 9 sample within the error of measurement. For Si- samples, those two values were always slightly higher as compared to PDMS 9 sample.

**Table 5.6. The values of \( \gamma_{\text{CA}} \) and \( W_i^{\text{eff}} \) for A- and Si- surfaces**

<table>
<thead>
<tr>
<th>Samples</th>
<th>( \gamma_{\text{CA}} ) a, ± 0.3 mJ/m²</th>
<th>( W_i^{\text{eff}} ) b, ± 0.5 mJ/m²</th>
<th>SiO₂ wt% in bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS 9</td>
<td>21.1</td>
<td>41.8</td>
<td>0</td>
</tr>
<tr>
<td>A-r1.2</td>
<td>21.6</td>
<td>41.1</td>
<td>0.80</td>
</tr>
<tr>
<td>A-r10</td>
<td>21.9</td>
<td>41.2</td>
<td>4.44</td>
</tr>
<tr>
<td>A-r30</td>
<td>22.5</td>
<td>41.7</td>
<td>8.64</td>
</tr>
<tr>
<td>A-r50</td>
<td>22.5</td>
<td>42.2</td>
<td>14.30</td>
</tr>
<tr>
<td>Si-r1.2</td>
<td>22.3</td>
<td>42.6</td>
<td>0.80</td>
</tr>
<tr>
<td>Si-r10</td>
<td>22.8</td>
<td>43.0</td>
<td>4.44</td>
</tr>
<tr>
<td>Si-r30</td>
<td>23.7</td>
<td>43.5</td>
<td>8.64</td>
</tr>
<tr>
<td>Si-r50</td>
<td>23.8</td>
<td>43.8</td>
<td>14.30</td>
</tr>
</tbody>
</table>

\( ^a \) calculated by using the advancing angles of water and methylene iodide.

\( ^b \) obtained by fitting the loading curve of JKR experiments.

Based on the CA values (Table 5.4) and \( W_i^{\text{eff}} \) values (Table 5.6) of A- and Si- surfaces, we plotted the contact angles with H₂O as a function of SiO₂ wt% in bulk, as shown in Figure 5.6. The plots of contact angle hysteresis, \( \Delta \theta \ (= \theta_{\text{adv}} - \theta_{\text{rec}}) \), as a function of SiO₂ wt% in bulk, are shown as Figure 5.7a. For A- surfaces, the contact angles are quite constant and very close to the contact angles of Ref-PDMS (see Table 5.4). The values of \( \theta_{\text{adv}}, \theta_{\text{rec}} \) and \( \Delta \theta \) are within the error of measurement independent of the amount of SiO₂ present in the bulk of these materials. This observation corresponds to
the absence of SiO₂ particles in the outermost layer of 1-2 nm thick, as shown previously. Apparently the polar groups at the surface of SiO₂ particles present below the top 1-2 nm layer are too far away to stretch out to the surface under the influence of the water at the surface.

**Figure 5.6.** Contact angles of water for A- and Si- surfaces as a function of SiO₂ wt % in bulk. The lines serve to guide the eye only.

![Figure 5.6.](image)

When we look at the Si- surfaces a completely different effect is observed. The values of θ_{adv}, θ_{rec} and Δθ are dependent on the amount of SiO₂ present in the bulk and show a clear trend with the concentration of SiO₂ (Figure 5.6 and Figure 5.7a). Both θ_{adv} and θ_{rec} values decrease but Δθ increases with increasing the concentration of SiO₂.

**Figure 5.7.** Plot of (a) contact angle hysteresis (θ_{adv} – θ_{rec}) and (b) W_{eff} as a function of SiO₂ wt% in bulk for A- and Si- samples. The lines serve to guide the eye only.

![Figure 5.7.](image)
This is in line with our previous conclusion that SiO$_2$ particles are present at the (almost) outermost top lay for the Si- surfaces. Above results show that CA measurements demonstrate the difference between the A- and Si- surfaces. However, this technique does not probe the difference of A- surfaces with a varying concentration of SiO$_2$ particles in the bulk.

Now we discuss the $W_i^{\text{eff}}$ values obtained from our JKR experiments. As shown in Figure 5.7b, the $W_i^{\text{eff}}$ values display a small but measurable difference for all samples. These values for the A- and Si- surfaces increase with an increase in the SiO$_2$ concentration in bulk, with slightly higher values for the Si- surfaces. Hence, our JKR experiments are able to probe the effect of SiO$_2$ particles below the top layer of 1-2 nm thick, showing that with JKR the $W_i^{\text{eff}}$ is a summation of a deeper top layer at the surface because of the larger penetration depth used in this measurement compared to CA measurements. Still the total amount of SiO$_2$ in this probed layer is likely to be lower for the A- samples than for the Si- samples, which is reflected in the lower $W_i^{\text{eff}}$ for the A- samples.

The effect of SiO$_2$ is relatively small on the $W_i^{\text{eff}}$ values obtained for the loading part of our JKR measurements. As will be discussed in the following section, this effect is much more dramatic when the unloading part of our JKR experiments is studied.

### 5.3.3.3. Unloading curves of JKR experiments

#### The values of $G^{\text{eff}}$

As described in Chapter 1, although theoretically the JKR model does not apply for hysteretic situations, in the literature researchers extend the JKR approach with the fracture mechanics [42] to study the adhesion hysteresis. The following equation

$$ G = \left( \frac{K a^3}{R} - P \right)^2 $$

is always used to compute comparable values of the energy release rate, $G$, for every point during the loading and unloading processes [43-46]. In this thesis, such effective
values calculated from our measurements according to equation 1.1, are denoted as “$G_t^{\text{eff}}$” and “$G_u^{\text{eff}}$” for loading and unloading curve, respectively, as discussed in previous chapters. Below we will discuss if, for our materials, these “$G_t^{\text{eff}}$” and “$G_u^{\text{eff}}$” can be used for quantitative comparison or not.

*Delay time* ($t_{\text{delay}}$)

Some interesting facts were observed during the unloading parts of our experiments. When the motor is activated to pull back the lens sample, the force recorded reduced at the same time with no time delay, as shown in Figure 5.8a (waiting 5 s) and Figure 5.8b (waiting 5 min). However, the contact between the lens and sheet samples may still be kept for some time until a certain negative force is reached. An example of experiments of the contact between a non-extracted PDMS 9 lens and Si-r30 sheet sample is given in Figure 5.9a (waiting 5 s) and Figure 5.9b (waiting 5 min). We define a delay time, $t_{\text{delay}}$, as the time difference between the last point of maximum force and the last point of maximum contact radius during the unloading part, as shown in Figure 5.9. During this interval, the image of contact circle was observed to become blurred. The results in Figure 5.9 suggest that equation 1.1 cannot be used anymore to calculate $G_u^{\text{eff}}$ quantitively.

![Figure 5.8a](image)

*Figure 5.8a.* Plot of force and displacement with time for Si-r30.

Lens: non-extracted PDMS 9, motor speed: 200 nm/s, waiting time: 5 s.
**Figure 5.8b.** Plot of force and displacement with time for Si-r30.
Lens: non-extracted PDMS 9, motor speed: 200 nm/s, waiting time: 5 min.

**Figure 5.9a.** Plot of force and contact radius with time for Si-r30.
Lens: non-extracted PDMS 9, motor speed: 200 nm/s, waiting time: 5 s.
In the following sections, the parameter $t_{\text{delay}}$ is used to demonstrate experimentally the hysteresis of tested samples, while $G^{\text{eff}}$ values are used to make a comparison, although not quantitively, between our results and literature data as well.

**Influence of waiting time and contact radius**

For self-adhesion of PDMS 9 samples, which is discussed in Chapter 4, a small hysteresis was observed and we attributed this to the bulk viscoelastic losses of the PDMS 9 sample. This hysteresis does not change with waiting time and different contact radii. However, we found that both the A- and Si- samples showed an increase in the adhesion hysteresis when a longer waiting time and/or a larger contact radius was used in the measurements. The delay time $t_{\text{delay}}$ at different maximum contact radius ($a_{\text{max}}$) and waiting times are listed in Table 5.7. Figure 5.10 shows the plot of $G^{\text{eff}}$ calculated with equation 1.1, as a function of contact radius. These results show that $G^{\text{eff}}_{ul}$ is strongly dependent on the time spent on contact, as well as $t_{\text{delay}}$. $G^{\text{eff}}_{ul}$ values seem to be smaller for A-r30 than for Si-r30, suggesting that hydrogen bonding may contribute to the measured hysteresis.
Table 5.7. \( t_{\text{delay}} \) at different maximum contact radius (\( a_{\text{max}} \)) and waiting times for A-r30 and Si-r30 samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Waiting time, s</th>
<th>( a_{\text{max}}, \mu m )</th>
<th>( t_{\text{delay}}, s )</th>
<th>( a_{\text{max}}, \mu m )</th>
<th>( t_{\text{delay}}, s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-r30</td>
<td>5</td>
<td>145</td>
<td>8</td>
<td>192</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>145</td>
<td>22</td>
<td>193</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>146</td>
<td>27</td>
<td>193</td>
<td>49</td>
</tr>
<tr>
<td>Si-r30</td>
<td>5</td>
<td>147</td>
<td>6</td>
<td>195</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>148</td>
<td>25</td>
<td>196</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>150</td>
<td>33</td>
<td>197</td>
<td>57</td>
</tr>
</tbody>
</table>

Figure 5.10. Plots of \( G^\text{eff} \) vs. \( a \) for A-r30 and Si-r30 surfaces.

Lens: non-extracted PDMS 9, motor speed: 200 nm/s.

As discussed previously, SiO\(_2\) particles are present close to the surface of all samples. The difference is that Si-* samples have more SiO\(_2\) than A-* samples in the top layer of several nanometers thickness. The –OH groups at the surface of SiO\(_2\) particles may stretch out to the interface between the PDMS 9 lens and the sheet sample when pressure is given to the system, hence hydrogen bonds may form at the interface. This is one of the most important mechanisms we propose to interpret the observed hysteresis. Another possible reason is the presence of unreacted –OH groups in the materials, which originates from two reasons. Firstly, the silanol-terminated PDMS was used to prepare the network. Secondly, the crosslinker TEOS is easily hydrolyzed. The unreacted –OH groups present close the surface may form hydrogen bonds when brought into contact with a PDMS 9 lens.
The influence of the contact time on the adhesion hysteresis, in case that temporary hydrogen bonds are formed at the interface, has been studied for different Si-OH surface \([43, 47, 48]\). These authors showed that hysteresis increased significantly with contact time, and attributed this to the structural reorganization of the interface caused by the formation of hydrogen bonds. They hypothesized that during contact time additional hydrogen bonds form, as the polymer relaxes near the interface, or that existing ones grow stronger. Baljon and co-workers \([49]\) proposed that an internal rearrangement as the reason for the increase in hysteresis with contact time. As a result of this new hydrogen bond configuration it may take more energy to separate the two contacting materials. Our case is somewhat different; the Si–OH groups are present close to the surface. Therefore, for the formation of hydrogen bonds, the –OH groups need to stretch out to the interface which means that the occurrence of a structural reorganization is necessary. After this, both the formation of new and stronger hydrogen bonds and the redistribution of the hydrogen bonds are possible reasons for the increase in hysteresis with contact time observed in our experiments.

Furthermore, the actual contact line may be different when different contact radii are reached, as shown in Scheme 5.2. Because of the influence of the SiO\(_2\) fillers which are present close to the surface, the contact can be regarded as between a smooth lens and a rough substrate, and the roughness of the substrate may influence the actual contact area. When a larger contact radius is reached under a larger load, the underlying SiO\(_2\) particles may indent deeper into the PDMS lens and increase the contact area, which is similar to a contact between a smooth lens and a rougher substrate compared to the contact at lower load. Hence, the actual contact area can be larger and more Si-OH groups can reach the interface. This will lead to a larger \(G_{\text{eff}}\) value and \(t_{\text{delay}}\) for a contact with a larger contact radius. Meanwhile, a relatively longer time is needed for a larger contact radius to be reached. Since the influence of contact time is very obvious (which will be shown in the next section in detail), this increase in contact time also contributes to the observed higher \(G_{\text{eff}}\) value and \(t_{\text{delay}}\).

**Scheme 5.2.** Schematic diagram of the side view contact line
Above presented $G_{ul}^{eff}$ values were calculated using equation 1.1 based on the JKR model under the non-equilibrium conditions used by us. Therefore these values are used only in a semi-quantitive way to make comparisons possible. Moreover, special care must be given for choosing measurement parameters, such as maximum external force (contact radius), loading / unloading speed, waiting time, etc. when comparing $G_{ul}^{eff}$ values.

**Adhesion hysteresis of A- and Si- surfaces**

Contacts between a non-extracted PDMS 9 lens and A- and Si- surfaces were made to study the adhesion hysteresis. The same contact radius was reached for both surfaces in order to exclude the contribution of contact radius on the hysteresis observed, as discussed in the previous section.

![Graphs showing adhesion hysteresis](image)

**Figure 5.11.** Plots of $G_{ul}^{eff}$ versus $a$ for A- and Si- surfaces prepared with different $r$ ratio($r = 1.2, 10, 30, 50$). Lens: non-extracted PDMS 9, motor speed: 200 nm/s, waiting time: 5 s.
### Table 5.8. Values of $t_{\text{delay}}$ for A- and Si- surfaces *

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a_{\text{max}}, \mu\text{m}$</th>
<th>$t_{\text{delay}}, \text{s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-r1.2</td>
<td>152</td>
<td>2</td>
</tr>
<tr>
<td>Si-r1.2</td>
<td>152</td>
<td>4</td>
</tr>
<tr>
<td>A-r10</td>
<td>157</td>
<td>7</td>
</tr>
<tr>
<td>Si-r10</td>
<td>158</td>
<td>15</td>
</tr>
<tr>
<td>A-r30</td>
<td>145</td>
<td>8</td>
</tr>
<tr>
<td>Si-r30</td>
<td>147</td>
<td>6</td>
</tr>
<tr>
<td>A-r50</td>
<td>146</td>
<td>8</td>
</tr>
<tr>
<td>Si-r50</td>
<td>146</td>
<td>10</td>
</tr>
</tbody>
</table>

* Waiting time: 5 s, motor speed: 200 nm/s.

The plot of $G^{\text{eff}}$ as a function of contact radius, $a$, is shown in Figure 5.11. For the same contact radius for A- and Si- surfaces, we found that the hysteresis for the Si-* surfaces is always higher than that for the A-* surfaces. This observation is, again, in agreement with our previous conclusion that the Si-* surfaces contain more silica in the top layer of several nanometer thickness. It is interesting to notice that such a difference in hysteresis is less obvious when the feed ratio, $r$, reaches the high end (e.g. $r = 30, 50$). This observation indicates that the influence of Si-OH groups on the hysteresis, even with a small amount, is dramatically large under our measurement conditions.

![Figure 5.11](image)

**Figure 5.12.** Plot of $t_{\text{delay}}$ as a function of SiO$_2$ wt% in bulk for A- and Si- samples.

The lines serve to guide the eye only.
The delay time $t_{\text{delay}}$ for the contact between a non-extracted PDMS 9 lens and A- and Si- surfaces with a waiting time of 5 s are listed in Table 5.8. Based on these data, we plotted the delay time $t_{\text{delay}}$ as a function of SiO$_2$ wt% in bulk, as shown in Figure 5.12. When similar contact radii were achieved for different SiO$_2$ concentrations, the $t_{\text{delay}}$ for A- surface appeared to reach a plateau when the concentration is larger than a value $\sim$ 4 wt%. The values of $t_{\text{delay}}$ for Si- surface did not show such a trend for a short waiting time. However, for $r = 30, 50$, $t_{\text{delay}}$ seemed to be close to the values for A-surface, in good agreement with our previous observation for calculated $G^{\text{eff}}$ values (Figure 5.11). These observations indicated that, for both A- and Si- surfaces, the adhesion for a short contact time is no longer dependent on the bulk SiO$_2$ concentration when the SiO$_2$ concentration reaches a certain value.

An important factor in determining the value of energy required to separate the two contacting materials is the areal density of the –OH groups which can form hydrogen bonding at the interface. The number of hydrogen bonds formed may be proportional to amount of Si–OH groups which are available for the bond formation. As we mentioned earlier, the major part of these –OH groups comes from the surface of in-situ precipitated SiO$_2$. It is reasonable to assume that the more SiO$_2$ present close to the surface, the more –OH groups are present and hence more hysteresis is expected. However, the situation is not as simple as this, because the number and strength of these hydrogen bonds may change to a large extent during the reconstruction of the interface. Furthermore, the number of –OH groups at the surface of SiO$_2$ also depends on the morphology of the precipitated SiO$_2$, namely the size and distribution of the SiO$_2$ phase in the material. The morphology of SiO$_2$ may be different at the surface when a different $r$ ratio is used to prepare the hybrid samples, and also different for A- and Si- samples even the same $r$ ratio is applied. Furthermore, we can not exclude the influence of the unreacted –OH groups present in the materials. These factors may be other reasons to explain why we do not observe an obvious high hysteresis for samples prepared with high $r$ ratio.

**Contact between A- and Si- surfaces and an extracted lens**

As discussed in chapter 4, the self-adhesion hysteresis of crosslinked PDMS samples increased after the sol fraction was extracted. Although the extraction of sol fraction from our PDMS/SiO$_2$ samples was not possible, we still conducted the adhesion experiments between the A- and Si- surfaces and an extracted PDMS 9 lens. The results with different waiting time are shown in Figure 5.13. We observed an increase in hysteresis for all samples after the lens was extracted. This observation, again,
indicated that the sol fraction present at the interface may partly mask the hysteresis, at least in the time scale of our experiments, in line with the conclusion in section 4.3.2.

**Figure 5.13.** Plot of $G^{\text{eff}}$ versus $a$ for the contact between A- and Si- surfaces and an extracted PDMS 9 lens. $r = 10, 30$.

### 5.4. Conclusions

PDMS-based inorganic/organic hybrid materials were prepared by the sol-gel method on Si wafer, Al and PS substrates. The surface roughness of hybrid surfaces made in contact with air (A-* surfaces) and different substrates (Si-* , PS-* and Al-* surfaces) were characterized by AFM. The results obtained by XPS and DCA analysis showed that surface structures of the hybrid surfaces made in contact with air and substrates are different. The former have a silica-free PDMS top layer of ~ 2 nm thick; while in
the latter cases SiO$_2$ is more likely located beneath the outermost atomic layer, and polar –OH groups at the surface of SiO$_2$ can easily stretch out to the outermost atomic layer when the surfaces contact with polar groups.

The JKR behavior of the contact between a PDMS 9 lens and A-* and Si-* surfaces prepared with different $r$ ratios was investigated in detail. From the loading parts, the elastic moduli and work or adhesion obtained from the loading curves are in good agreement with the results measured by micro-indentation and contact angle analysis, respectively.

Adhesion hysteresis was studied intensively using the unloading parts. The values of $l_{\text{delay}}$ and the calculated $G_{\text{eff}}$ values were used to make semi-quantitive comparison of results. Both A-* and Si-* surfaces showed an increase in hysteresis when larger contact radius and/or longer waiting time are applied, and this is attributed mainly to the formation of hydrogen bonds at the interface. For the samples prepared with the same $r$ ratio, Si- surfaces display higher adhesion hysteresis as compared to A-* surfaces, due to the higher concentration of SiO$_2$ in the top layer of several nanometer thickness. This difference is more obvious when a small feed ratio $r$ is applied. Extraction of the sol fraction from the PDMS lens enhanced the hysteresis.

Comparison between CA hysteresis and JKR hysteresis is made in this chapter. CA hysteresis showed no difference for A- surfaces but a small difference for Si- samples with a variation in the feed ratio of $r$, indicating that CA analysis probes the surface property of the outermost a couple of atom layers. On the other hand, much more information can be obtained from the JKR experiments. Several factors can influence the observed hysteresis, such as the maximum contact radius (or load), waiting time, feed ratio $r$ of the samples (filler concentration), etc. The JKR technique probes the adhesion and interfacial properties between two solid materials with a larger penetration depth than that of CA analysis.

References

Adhesion study on crosslinked PDMS containing in-situ precipitated SiO$_2$

Chapter 6

Effect of surface modification on adhesion of crosslinked PDMS materials

6.1. Introduction

Since their introduction in the 1960’s, polysiloxanes, or silicone rubbers, have steadily gained market share from porcelain and glass as outdoor insulation and protective materials [1-4], anticorrosion, antifouling [5], soft lithography [6-11], photo-finishing [12], microfluidic devices [13-14], biomedical practice [15-18]. In many applications, especially in soft lithography, microfluidic devices and biomedical applications, a modification of the PDMS surfaces is needed to achieve a desired adhesion property with other (polymer) materials.

It has long been recognized that in order to modify the surface properties of PDMS, various techniques can be utilized. Among these techniques, ultraviolet (UV) radiation [19-20], ultraviolet/ozone (UV/O$_3$) treatment [21-24] and oxygen plasma [25-29] are widely employed for this purpose. It was previously shown that when exposed to UV/O$_3$, crosslinked PDMS surfaces undergo irreversible surface chemical changes. According to the literature, modified PDMS surfaces are more hydrophilic and contain polar groups such as –OH groups. Moreover, the PDMS surfaces are converted onto a thin silica-like layer with a thickness of several tens of nanometer. After surface modification with UV/O$_3$ or oxygen plasma, the PDMS surface becomes hydrophilic. However, the surface hydrophilicity is lost with time after the treatment. This change from a hydrophilic to a hydrophobic surface is often referred to as “hydrophobicity recovery” [30]. It is believed that migration of low molecular weight PDMS chains plays an important role in this hydrophobicity recovery [31-33]. Another mechanism which contributes is the reorientation of polar groups from the surface into the bulk [27, 29, 34-35]. This mechanism is important when mild oxidation conditions, such as UV/O$_3$ and UV radiation, are used to modify the PDMS surface, in which only a few number of the polymer side groups are oxidized.

The oxidation processes and their effect on PDMS surfaces, after exposure to UV/O$_3$
or oxygen plasma, have been intensively investigated using X-ray photoelectron spectroscopy (XPS) and water contact angle (CA) measurements. Quite often CA measurements and atomic force microscopy (AFM) are used to study the hydrophobicity recovery. However, the adhesion property between modified PDMS surfaces and other solid materials are seldom reported. Oláh et al. [36] studied the adhesion between UV/O$_3$ treated PDMS lenses and thin films of two commercial product packages with different filler composition. They reported different behaviours for samples with variation in chemical composition. However, no adhesion study between treated PDMS and other materials is given. Therefore, we studied the adhesion behaviour of UV/O$_3$ treated PDMS materials using the JKR technique as the main method.

Another trigger for this investigation is the necessity of surface modification of PDMS when layered materials are studied in the JKR measurements. For such purposes, normally a thin layer of a material of interest is deposited on the surface of a PDMS substrate. In order to promote the adhesion between the PDMS substrate and other materials of interest, generally the surface of the PDMS substrate is oxidized using UV/O$_3$ or oxygen plasma to introduce polar groups [37-40].

In this chapter we study the adhesion behaviour of surface modified crosslinked PDMS using the JKR technique. The results of the contact between UV/O$_3$ treated PDMS lenses and flat sheets of non-treated PDMS, polystyrene (PS) and Indium Tin Oxide (ITO) are presented.

### 6.2. Experimental

**6.2.1. Materials**

Crosslinked PDMS 9 lenses and sheets were prepared according the procedure described in Chapter 2.2. All PDMS lenses and sheets were used without extraction.

PS (Polymer Laboratories, $M_w = 120$ kg/mol, $M_w/M_n = 1.13$) was dissolved in toluene to form a 2 wt% solution. After filtered using 0.2 µ Millipore filters, this solution was spin coated onto glass slide and then annealed under vacuum at 140 °C for 2 hours. Film thicknesses were in the range 120 – 140 nm. A thick PS film (~ 30 µm) was also prepared for elastic modulus measurements.

The ITO layer on glass samples were kindly provided by Philips, Eindhoven. The ITO
layers were deposited on glass substrates in a Leybold sputter system. The target composition was 90 wt% In$_2$O$_3$ mixed with 10 wt% Sn$_2$O$_3$. The sputter power was 600 W. The deposition was started at room temperature and ended at approximately 100 °C. The deposition rate was 20 nm/min while the substrate carrier was rotated at 10 rpm. The thickness of the ITO layer was about 1 µm.

6.2.2. UV/O$_3$ treatment of PDMS lenses

The UV/O$_3$ treatment of PDMS 9 lenses used for the JKR experiments was performed in a commercial UV/O$_3$ cleaner (RP – 100 UV-Ozone Photoreactor). This equipment contains a low-pressure mercury UV-light, generating UV radiation wavelengths of $\lambda = 185$ (1.5 mW/cm$^2$) and 254 nm (15 mW/cm$^2$). The distance between the UV source and the PDMS samples was about 25 mm. All samples were used for all measurements within 3 hours after treatment. Samples after treatment were denoted as “PDMS 9$_{ox}$”, with a number in the superscript indicating the exposure time. For example, PDMS 9$_{ox-15}$ is a sample treated with UV/O$_3$ for 15 min.

PDMS 9 flat sheets prepared from the same formulation as lenses were also treated with UV/O$_3$. These sheet samples were used only for roughness measurements and contact angle analysis.

6.2.3. Methods

The nanoscale surface roughness of all sheet samples were measured using AFM NTEGRA (NT-MTD, Moscow, Russia) in the intermittent contact mode with Si-cantilevers, spring constant $k = 5.5$ N/m (NSG01, NT-MDT, Moscow, Russia). In general, a sample area of 1 x 1 µm was scanned. The measurements were performed in air at room temperature at a humidity of 45-50%. The root mean square roughnesses were calculated from AFM height images of the PDMS flat sheets.

Dynamic contact angle (DCA) analyses were performed in air at room temperature using the sessile drop method with the OCA30 apparatus (Dataphysics Instruments). Distilled water was used as the probe liquid. All advancing and receding contact angles were the average value of at least five measurements on different positions of the sheets.

Adhesion experiments were performed with our JKR apparatus (see Chapter 2). A motor speed of 200 nm/s was always applied. All samples were measured at least
three times. Various waiting times between the loading and unloading part of an experiment cycle were applied.

6.3. Results and discussions

6.3.1. UV/O\textsubscript{3} treatment of PDMS 9 surfaces

6.3.1.1. Contact angle measurements

The advancing and receding contact angles with water of PDMS 9 flat sheets as a function of UV/O\textsubscript{3} exposure time were shown in Figure 6.1. The advancing contact angle showed a slow and gradual decrease with an increase in exposure time, while the receding contact angles displayed much more rapid decrease with exposure time.

It is known that the advancing contact angles are more associated with the low surface energy regions and the receding angles are associated with the high surface energy regions on heterogeneous polymer surfaces [29, 41]. Our data in Figure 6.1 suggest the introduction of polar groups at the surface after treatment. The slow change and relatively high values of the advancing angles after treatment indicates that the surfaces of our PDMS 9 samples were only partially oxidized.

![Contact angle vs UV/O\textsubscript{3} exposure time](image)

**Figure 6.1.** Advancing and receding contact angles with water of PDMS 9 sheets as a function of UV/O\textsubscript{3} exposure time.

It is widely accepted that the contact angle hysteresis depends on the roughness, heterogeneity, and molecular mobility (reorientation of functional groups) on the probed surface region [42-43]. We observed an increase in the contact angle hysteresis with exposure time. As will be shown in the next section, the roughnesses of these
surfaces are very low and decrease with UV/O$_3$ treatment time, showing a smoother surface after treatment. Therefore, the difference in contact angle hysteresis is also an indication of introduction of polar groups which have the possibility of reorientation, depending on the surrounding medium. This increase in contact angle hysteresis is also an indication of partial oxidization of the PDMS 9 surfaces within our exposure time scale.

6.3.1.2. Roughness
The root mean square roughness of our PDMS 9 samples before and after the treatment are listed in Table 6.1. The surface roughness decreased with an increase in UV/O$_3$ treatment time, in line with literature [23, 26, 36]. Such smooth surfaces indicate that the roughness of our PDMS 9 surfaces before and after treatment do not play a role in the contact angle measurements. Also we expect almost no influence of roughness on our JKR results which will be presented in the next section.

<table>
<thead>
<tr>
<th>Samples</th>
<th>PDMS 9</th>
<th>PDMS 9$_{ox-15}$</th>
<th>PDMS 9$_{ox-60}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_q$, nm</td>
<td>0.92</td>
<td>0.69</td>
<td>0.52</td>
</tr>
</tbody>
</table>

6.3.2. JKR results
The loading curves of our JKR measurements on the contact between a treated PDMS 9 lens and a sheet sample were studied. The sheet samples studied were PDMS 9, PS (120-140 nm thickness) on glass and ITO (1 µm thickness) on glass. Before we consider the JKR results, it is necessary to evaluate the elastic modulus and roughness ($R_q$, root mean square roughness) values of the sheet samples used in our experiments. These data are listed in Table 6.2.

<table>
<thead>
<tr>
<th></th>
<th>PDMS 9</th>
<th>PS</th>
<th>ITO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic modulus, MPa</td>
<td>$1^a$</td>
<td>$3,500^b$</td>
<td>$120,000^c$</td>
</tr>
<tr>
<td>Roughness, nm</td>
<td>0.92</td>
<td>1.65</td>
<td>35</td>
</tr>
</tbody>
</table>

$^a$ measured by micro-indentation measurements on a PDMS sheet (1 mm) assuming the poisson’s ratio as 0.5; $^b$ measured by micro-indentation measurements on a PS coating (30 µm) on glass assuming the Poisson’s ratio as 0.34 [44]; $^c$ estimated value [45].
### 6.3.2.1. Loading part of the JKR experiments

PDMS 9 lenses were treated for 15, 30 and 60 min, respectively. The values of $K_{l}^{\text{eff}}$ and $W_{l}^{\text{eff}}$ were obtained by fitting the loading curves to equation 1.4. The value of $G_{l}^{\text{eff}}$ at each point was calculated using $K_{l}^{\text{eff}}$ according to equation 1.1 and averaged. All these values are listed in Table 6.3.

**Table 6.3.** $K_{l}^{\text{eff}}$ and $W_{l}^{\text{eff}}$ values obtained from the loading curves for JKR experiments between treated PDMS lenses and sheets of PDMS 9, PS and ITO $^*$.  

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Lens</th>
<th>Sheet</th>
<th>$K_{l}^{\text{eff}}$ (± 0.04 MPa)</th>
<th>$W_{l}^{\text{eff}}$ (± 1.0 mJ/m$^2$)</th>
<th>$G_{l}^{\text{eff}}$ average (± 1.5 mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PDMS 9</td>
<td>PDMS 9</td>
<td>0.90</td>
<td>41.8</td>
<td>41.5</td>
</tr>
<tr>
<td>2</td>
<td>PDMS$_{\text{ox-15}}$</td>
<td>PDMS 9</td>
<td>0.90</td>
<td>42.8</td>
<td>42.0</td>
</tr>
<tr>
<td>3</td>
<td>PDMS$_{\text{ox-30}}$</td>
<td>PDMS 9</td>
<td>0.89</td>
<td>43.1</td>
<td>43.0</td>
</tr>
<tr>
<td>4</td>
<td>PDMS$_{\text{ox-60}}$</td>
<td>PDMS 9</td>
<td>0.87</td>
<td>42.0</td>
<td>42.0</td>
</tr>
<tr>
<td>5</td>
<td>PDMS 9</td>
<td>PS</td>
<td>1.80</td>
<td>44.1</td>
<td>44.0</td>
</tr>
<tr>
<td>6</td>
<td>PDMS$_{\text{ox-15}}$</td>
<td>PS</td>
<td>1.90</td>
<td>43.0</td>
<td>42.5</td>
</tr>
<tr>
<td>7</td>
<td>PDMS$_{\text{ox-30}}$</td>
<td>PS</td>
<td>1.78</td>
<td>42.6</td>
<td>42.2</td>
</tr>
<tr>
<td>8</td>
<td>PDMS$_{\text{ox-60}}$</td>
<td>PS</td>
<td>1.71</td>
<td>39.3</td>
<td>39.1</td>
</tr>
<tr>
<td>9</td>
<td>PDMS 9</td>
<td>ITO</td>
<td>1.91</td>
<td>45.3</td>
<td>45.1</td>
</tr>
<tr>
<td>10</td>
<td>PDMS$_{\text{ox-15}}$</td>
<td>ITO</td>
<td>1.94</td>
<td>35.1</td>
<td>35.0</td>
</tr>
<tr>
<td>11</td>
<td>PDMS$_{\text{ox-30}}$</td>
<td>ITO</td>
<td>1.81</td>
<td>24.5</td>
<td>24.5</td>
</tr>
<tr>
<td>12</td>
<td>PDMS$_{\text{ox-60}}$</td>
<td>ITO</td>
<td>1.51</td>
<td>8.5</td>
<td>8.6</td>
</tr>
</tbody>
</table>

* The ± sign indicates the sample standard deviation using 3-5 data points.

First we consider the adhesion between an untreated PDMS 9 lens and sheet samples (No. 1, 5 and 9). The higher values of $K_{l}^{\text{eff}}$ of about 1.8 MPa for a PS sheet and ITO sheet, compared to the value of 0.9 MPa for the PDMS-PDMS contact, are attributed to the much higher elastic modulus value (Table 6.2) for the PS and ITO sheet according to equation 1.2. The $W_{l}^{\text{eff}}$ and $G_{l}^{\text{eff}}$ values for a contact between an untreated PDMS 9 lens and a PS sheet (No. 5) are ~ 44 mJ/m$^2$, in good agreement
with the literature data [46-47]. The $W_i^{\text{eff}}$ and $G_i^{\text{eff}}$ value for a contact between an untreated PDMS 9 lens and ITO sheet (No. 9) are very similar to the values observed for a PS sample (No. 5), and close to the values for a PDMS 9 sheet (No. 1). Hence it is very likely that apart from a small contribution for viscoelastic losses in the PDMS 9 lens, these values are (almost) equal, within the error of measurement, to the thermodynamic work of adhesion, $W$. This is in line with the adhesion observations made in practice that for PDMS materials adhesion is very similar and weak for a broad range of different contacting materials, the main reason being that mainly van der Waals interactions are occurring. Apparently the contribution of other factors, such as hydrogen bonding which will be discussed later on, to the loading part is small under the measurement conditions used here. This is in agreement with our previous observation for PDMS sheets containing SiO$_2$ fillers as discussed in Chapter 5.

Now we move to the cases where a treated PDMS 9 lens is used. The $K_i^{\text{eff}}$, $W_i^{\text{eff}}$ and $G_i^{\text{eff}}$ values for the contact between a PDMS$_{ox}$ lens and a PDMS 9 sheet (No. 2-4) appeared to be independent of the length of UV/O$_3$ exposure time, very similar to the values for the self-adhesion of PDMS 9 samples (No. 1). For the contact between a PDMS$_{ox}$ lens and a PS sheet, these values show no large difference when the UV/O$_3$ exposure time of 15 min (No. 6) and 30 min (No. 7) were used.

When an ITO sheet was used (No. 10-12) in contact with a treated PDMS lens, the $W_i^{\text{eff}}$ and $G_i^{\text{eff}}$ values decrease with the exposure time of the PDMS 9 lens, while the value of $K_i^{\text{eff}}$ is approximately constant, only for an exposure time of 60 min (No. 12) a small decrease is noticed.

As mentioned above, in some cases when a PS and an ITO were used, the $K_i^{\text{eff}}$ (No. 8, 12), $W_i^{\text{eff}}$ and $G_i^{\text{eff}}$ (No. 8, 10-12) values calculated from the JKR model showed a dependency on treatment time. We believe that this change is caused by the deviation of our lens-sheet system from the requirements of the JKR model. The JKR model holds for a purely elastic contact between two smooth and homogeneous solids. Therefore this model is no longer valid if the deformation zone is not purely elastic.
and/or homogeneous. A rough surface may also cause the deviation. In such cases, the JKR model is not directly applicable and, if possible, some corrections have to be made.

It is known that after the treatment with UV/O$_3$, the surface of PDMS is (partially) converted to silica-like layer with a thickness of a couple of dozens of nanometers. This oxidized thin layer has a different chemical composition and mechanical properties. For instance, this oxidized layer contains silica phases and polar groups, such as –OH groups. The oxidized layer contains more silica phases and could be thicker with the increase in the UV/O$_3$ exposure time. The elastic modulus of this thin layer is very likely to increase to a large extent as compared with the “original” material because of the presence of such inorganic phases. Therefore, the treated lens is no longer homogeneous and isotropic and such a “layered” structure may strongly influence the JKR results when the lens is deformed. When a treated lens is contact with a soft PDMS 9 sheet, both the lens and sheet sample will deform. However, when a much harder sheet sample is used, for instance the PS and ITO samples in our cases, the deformation only occurs in the lens. Literature has demonstrated that when the JKR model is applied on a multi-layer elastic system, corrections have to be included based on the data of thickness and elastic modulus of each layer [48-49]. The authors of these papers worked with a hard sphere in contact with a layered elastic half-space, which is comparable to the treated lens in contact with a hard sheet in our study. However, in our experiments where a treated lens was used, the deformation is likely not purely elastic, especially when the lens was treated for a longer time.

Another important parameter is the roughness of the sheet samples, which was shown to strongly influence the actual contact area and the measured work of adhesion values [50-52]. This may be relevant in the case of a ITO sheet which has a relatively high surface roughness (Table 6.2).

Afore mentioned possible reasons will be discussed also in the next section, where the unloading parts of our experiments are interpreted.

### 6.3.2.2. Unloading parts

Similar to Chapter 5.3.3.3, the delay time, $t_{\text{delay}}$, is defined as the time difference between the last point of maximum force and the last point of maximum contact radius during the unloading experimental part. An example is shown in Figure 6.2.
Effect of surface modification on adhesion of crosslinked PDMS materials

Figure 6.2a. Plot of force and displacement versus time.
Lens: PDMS 9_{ox-15}, sheet: PDMS 9 (No. 2), motor speed: 200 nm/s, waiting time: 5 s.

Figure 6.2b. Plot of force and contact radius versus time.
Lens: PDMS 9_{ox-15}, sheet: PDMS 9 (No. 2), motor speed: 200 nm/s, waiting time: 5 s.

This parameter is used as well as $G^{\text{off}}$ values calculated according to equation 1.1, to discuss the unloading data.

Effect of UV/O\textsubscript{3} exposure time
The $t_{\text{delay}}$ values for contact between a PDMS\textsubscript{ox} lens and a PDMS 9 sheet are listed in Table 6.4. The self-adhesion between PDMS 9 lens and sheet displayed almost no
time delay, while after surface treatment using UV/O\textsubscript{3}, the values for \( t_{\text{delay}} \) were substantial. For treated PDMS\textsubscript{ox} lenses, the values decreased with an increase in treatment time.

**Table 6.4.** \( t_{\text{delay}} \) for the unloading between a PDMS\textsubscript{ox} lens and a PDMS 9 sheet*.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lens</td>
<td>PDMS 9</td>
<td>PDMS\textsubscript{ox-15}</td>
<td>PDMS\textsubscript{ox-30}</td>
<td>PDMS\textsubscript{ox-60}</td>
</tr>
<tr>
<td>( t_{\text{delay}} ), s</td>
<td>&lt; 1</td>
<td>22.1</td>
<td>16.5</td>
<td>8.7</td>
</tr>
</tbody>
</table>

*All experiments were performed at a motor speed of 200 nm/s and a waiting time of 5 s.

**Figure 6.3.** Plot of \( G_{\text{eff}} \) versus \( a \) for adhesion between a PDMS\textsubscript{ox} lens and a PDMS 9 sheet (experimental No. 2-4). Motor speed: 200 nm/s, waiting time: 5 s.

For each measurement, the \( G_{\text{eff}} \) values at each point along the loading and unloading curve were calculated according to equation 1.1, as was done in the previous chapters. The plot of \( G_{\text{eff}} \) as a function of contact radius, \( a \), is shown in Figure 6.3, for the contact between a PDMS\textsubscript{ox} lens and a PDMS 9 sheet. Although the \( G_{\text{eff}} \) values were more or less constant and the same, the \( G_{\text{eff}} \) values were different and not constant. Hysteresis was observed in all cases, indicating adhesion promotion after the lens was treated. This can be explained by the introduction of polar groups, such as –OH.
groups, at the surface of the PDMS lens by UV/O\textsubscript{3} exposure, and further formation of H-bonding when such surface is made in contact with another PDMS surface. Comparing the $t_{\text{delay}}$ values in Table 6.4 and $G_{ul}^{\text{eff}}$ values in Figure 6.3, we observe that $t_{\text{delay}}$ and $G_{ul}^{\text{eff}}$ generally showed the same trend, i.e., the larger the $t_{\text{delay}}$, the larger the hysteresis. These data strongly suggest that adhesion between PDMS materials can be optimized by application of UV/O\textsubscript{3} treatment. However, the treatment time is critical. When a longer treatment time is applied, adhesion is less promoted.

For the contact between a PDMS\textsubscript{ox} lens and a PS sheet, $t_{\text{delay}}$ values are listed in Table 6.5. The plot of $G_{ul}^{\text{eff}}$ as a function of contact radius, $a$, is shown in Figure 6.4b, for the contact between a PDMS\textsubscript{ox} lens and a PS sheet. Compared to the case when a PDMS 9 lens without treatment was used (No. 5, see Figure 6.4a), the PDMS surface treatment within 30 min appeared to give no adhesion promotion. Unlike the PDMS\textsubscript{ox}–PDMS interface, at the PDMS-PS interface, only Van der Waals forces are present. No other interaction is introduced, after treatment, for the PDMS\textsubscript{ox}–PS interface. Therefore no adhesion promotion is expected. We attributed the small hysteresis, observed for the contact between a PDMS 9 lens and a PS sheet, to the bulk viscoelastic losses of the PDMS lens itself, which was discussed in Chapter 4 already.

Again, the $t_{\text{delay}}$ and $G_{ul}^{\text{eff}}$ values were in line with each other: a small number for $t_{\text{delay}}$ corresponds with a small value for the calculated $G_{ul}^{\text{eff}}$. The hysteresis resulting from the bulk viscoelastic losses of the lens seemed to be somewhat larger than for the non-treated PDMS 9 lens and sheet (~ 12 %, see Chapter 2) measured under the same conditions. In line with these findings are the somewhat lower $t_{\text{delay}}$ values for the latter case (Table 6.4 and Table 6.5).

| Table 6.5. Values of $t_{\text{delay}}$ for the unloading between a PDMS\textsubscript{ox} lens and a PS sheet*. |
|----------------|----------------|----------------|----------------|
| Exp. No.       | 5              | 6              | 7              | 8              |
| Lens           | PDMS 9         | PDMS\textsubscript{ox-15} | PDMS\textsubscript{ox-30} | PDMS\textsubscript{ox-60} |
| $t_{\text{delay}}$, s | 2.4            | 2.2            | 3.0            | 3.9            |

*All experiments were performed at a motor speed of 200 nm/s and a waiting time of 5 s.
When the PDMS 9 lens was treated for 60 min (No. 8), the values of both $G_{ul}^{\text{eff}}$ and $G_{l}^{\text{eff}}$ were different as compared with those treated for a shorter treatment time. A slight adhesion promotion is suggested, based on the somewhat higher $G_{ul}^{\text{eff}}$ value and the lower $G_{l}^{\text{eff}}$ value. However, the reliability of these values is doubtful for the following reasons. Firstly, a lowering of the $G_{l}^{\text{eff}}$ value is difficult to understand,
unless we assume that the van der Waals interactions between the oxidized PDMS lens surface and the PS surface is smaller and/or the contact between the oxidized PDMS lens and the PS surface is less intimate than for an untreated lens. However, this is unlikely because such a lowering of $G^{\text{eff}}_l$ value was not found for the cases (No. 6 and 7) when the PDMS lens was treated for a shorter time, and both surfaces and PS and a treated PDMS lens were quite smooth. Secondly, the surface treatment of the PDMS 9 lens by UV/O$_3$ introduces an oxidized thin layer which might not be purely elastic. Thirdly, $K^{\text{eff}}_l$ may be no longer constant within the whole indentation depth. However, to calculate $K^{\text{eff}}_l$ and $G^{\text{eff}}_l$ using equation 1.4 and equation 1.1, a purely elastic behaviour and a constant $K^{\text{eff}}_l$ were assumed.

For the contact between a treated and non-treated PDMS 9 lens and an ITO sheet, $t_{\text{delay}}$ values are listed in Table 6.6. The plot of $G^{\text{eff}}$ as a function of contact radius, $a$, is shown in Figure 6.5a and 6.5b for a non-treat PDMS 9 lens and PDMS$_{\text{ox}}$ lens, respectively.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lens</td>
<td>PDMS 9</td>
<td>PDMS$_{\text{ox}}$-15</td>
<td>PDMS$_{\text{ox}}$-30</td>
<td>PDMS$_{\text{ox}}$-60</td>
</tr>
<tr>
<td>$t_{\text{delay}},$ s</td>
<td>5.1</td>
<td>29.9</td>
<td>20.8</td>
<td>13.4</td>
</tr>
</tbody>
</table>

*All experiments were performed at a motor speed of 200 nm/s and a waiting time of 5 s.

The $G^{\text{eff}}$-a plot for the contact between a PDMS 9 lens without treatment and an ITO sheet was shown in Figure 6.5a. When we compare the contact between a non-treated PDMS lens and a PDMS 9 (No. 1) and PS sheet (No. 5), an increase in $G^{\text{eff}}_l$ and hysteresis was observed. Also the $t_{\text{delay}}$ values were larger. This suggests that, apart from the bulk viscoelastic losses of the lens, the rearrangement of hydrogen bonding at the PDMS – ITO interface and/or the roughness of the ITO surface may contribute to the adhesion hysteresis.
Figure 6.5a. Plot of $G^{\text{eff}}$ versus $a$ for a PDMS 9 lens and an ITO sheet (No. 9).

Figure 6.5b. Plot of $G^{\text{eff}}$ versus $a$ for a PDMS$_{\text{ox}}$ lens and an ITO sheet (No. 10-12).

Waiting time: 5 s.

The plot of $G^{\text{eff}}$ as a function of contact radius, $a$, was shown in Figure 6.5b, for the contact between a PDMS$_{\text{ox}}$ lens and an ITO sheet. Larger hysteresis was observed after the surface treatment of the PDMS lenses, indicating a promotion of the adhesion. However, the absolute $G^{\text{eff}}_{\text{ul}}$ values could not be used to compare the influence of exposure time directly, for the $G^{\text{eff}}_{\text{ul}}$ values were calculated by taking a constant value of $K^{\text{eff}}_l$ from the loading curve which was doubtful. As was discussed
previously, another important factor may be the non-elastic component of the oxidized layer of the PDMS 9 lenses after treatment, which was not included in equation 1.1 and 1.4 which we used to calculate these values.

It is interesting to notice that for the contact between a treated PDMS and ITO surface, a lowering of $G'_G$ value, which became larger when the UV/O3 treatment time increased, especially for a treatment time of 60 min. This was combined with a lower adhesion hysteresis and lower $t_{\text{delay}}$. The oxidized layer contains more inorganic silica phases for such a treatment time. Hence, the roughness of the ITO surface may influence the actual contact area, which could also lead to an error in using equation 1.1 and 1.4.

In the next chapter of this thesis, a thin layer of PS and ITO will be deposited on the surfaces of PDMS lenses. The above results provided useful information for the necessity of surface treatment on the PDMS substrates, in order to obtain good adhesion between such a thin layer and the PDMS lens.

**Effect of waiting time**

A waiting time of 5 min was applied in our experiments to study the effect of contact time. The $G'_G - a$ plot is shown as Figure 6.6, for the contact between a PDMS$_{\text{ox-15}}$ lens and a PDMS 9 (Figure 6.6a), PS (Figure 6.6b) and ITO (Figure 6.6c) sheet sample, respectively. The values of $G'_G$ was found to increase when a waiting time of 5 min was applied, as compared with 5 s. For the PDMS$_{\text{ox-15}}$–PDMS 9 interface (Figure 6.6a), we believe that the increase in hysteresis for a longer waiting time was caused by the rearrangement of the hydrogen bonding at the interface. For the PDMS$_{\text{ox-15}}$–ITO interface (Figure 6.6c), apart from the hydrogen bonding, the roughness of the ITO sheet might be an important factor. After waiting for a longer time, a larger contact area might be reached and a maximum contact area could be reached if a sufficient contact time is provided under the force applied.
Figure 6.6a. Plot of $G^{\text{eff}}$ versus $a$ for a PDMS$_{ox-15}$ lens and a PDMS 9 sheet.

Figure 6.6b. Plot of $G^{\text{eff}}$ versus $a$ for a PDMS$_{ox-15}$ lens and a PS sheet.

Figure 6.6c. Plot of $G^{\text{eff}}$ versus $a$ for a PDMS$_{ox-15}$ lens and an ITO sheet.
6.4. Conclusions

The influence of surface modification of crosslinked PDMS materials on the adhesion behaviour was studied. Surface modification was performed using an UV/O$_3$ treatment. Contact angle and AFM measurements show that the surface of PDMS contained polar groups such as –OH groups and became smoother after treatment.

The adhesion between non-treated and UV/O$_3$ treated PDMS 9 lenses and flat sheets of non-treated PDMS, PS and ITO was investigated using the JKR model. For the loading part, the effective elastic constant ($K_i^{\text{eff}}$) and effective work of adhesion ($W_i^{\text{eff}}$ and $G_i^{\text{eff}}$) values were almost equal for the contact of PDMS$_{ox}$–PDMS 9 (No. 1-4). Moreover, these values were very similar for most of the PDMS$_{ox}$–PS cases (No. 5-7) and for PDMS–ITO case (No. 9). This suggests that for these lens–sheet combinations the thermodynamic work of adhesion can be measured under the chosen measuring conditions.

For the PDMS$_{ox}$-60-PS and all the PDMS$_{ox}$–ITO combinations, different values were found which were sometimes combined with an unexpected decrease in $K_i^{\text{eff}}$, suggesting that non-elastic and inhomogeneous deformation in the contact zone may strongly influence the calculation of $K_i^{\text{eff}}$, $W_i^{\text{eff}}$ and $G_i^{\text{eff}}$. Roughness may be also important for the PDMS$_{ox}$–ITO system.

For the PDMS$_{ox}$–PS system the effect of the UV/O$_3$ treatment and waiting time during experiments on the $G_i^{\text{eff}}$ and $t_{\text{delay}}$ values was small. The observed adhesion hysteresis could be attributed mainly to the bulk viscoelastic losses in the PDMS$_{ox}$ lenses.

Using a PDMS$_{ox}$ lens in contact with a sheet of untreated PDMS and ITO in our JKR experiments, the adhesion hysteresis increased considerably and further increased with a longer waiting time. This can be attributed to the formation and rearrangement of hydrogen bonding at the interface. However, a longer UV/O$_3$ treatment time led to a lowering of adhesion.

Our JKR measurements on the contact between UV/O$_3$ treated PDMS lens and
different sheet materials show that useful information can be obtained about the adhesion promotion of PDMS materials by surface modification and how to optimize such modification for specific situations. Care has to be taken in comparing $K_{eff}$, $W_{eff}$ and $G_{eff}$ values calculated directly using the JKR model. Several factors which are not considered in the JKR model, such as non-elastic losses and heterogeneity in the deformation zone and roughness, may make these calculated values only reliable in a semi-quantitative way.

References

Effect of surface modification on adhesion of crosslinked PDMS materials

Chapter 7

Application of thin layers in JKR experiments

7.1. Introduction

Interfacial energy between solids is a property of solids in contact, and the only direct route to the experimental determination of this property is to bring the two solids into contact [1]. Contact mechanics is the study of the mechanics of solids spreading their interfacial area under load [2]. The JKR theory has been successfully applied to investigate the work of adhesion and interfacial energy via contact mechanics. This technique is well-suited for the contact between two solids where at least one of the solids is relatively soft, such as rubbery materials [3-10].

The extension of the JKR technique to solid polymers, particularly glassy and semicrystalline polymers, is limited, because these materials lack linear elasticity which is required by the JKR theory. They deform viscoelastically and plastically with substantial energy dissipation. Besides, these polymers often have a modulus higher than is convenient to measure significant increase in contact radius in the linear contact mechanics regime. Tirrell’s group has pioneered the adhesion between these polymeric surfaces using the JKR technique [1, 11-14]. The method is to deposit a thin polymer film (~ 100 nm) on a soft PDMS or other elastomer substrate and make a composite with the surface layer of the material of interest and a low bulk modulus.

The deposition of an inorganic thin layer on a soft substrate and its use in an adhesion study using the JKR technique were hardly addressed in the literature. Only Cho et al. [15] sputtered a thin indium tin oxide (ITO) onto both an atomic force microscopy (AFM) tip and a poly(dimethylysiloxane) (PDMS) lens. They obtained, using JKR model, relatively low values of work of adhesion for the contact between an ITO coated PDMS lens and a self-assembled monolayer of various functional groups on silicon wafers. They proposed to use a multiplying factor to correct their results.

In this chapter we deposit organic and inorganic thin layers on crosslinked PDMS 9 lenses and sheets to study the adhesion between polymers and inorganic materials, using our newly built JKR apparatus. Polystyrene (PS) and ITO were chosen as model
thin layers because of their wide application and ease of preparation of thin films, whereas also a few experiments were done using commercial polyester films.

7.2. Experimental

7.2.1. Materials

7.2.1.1. PS thin layer on PDMS substrates

PS (Polymer Laboratories, $M_w = 120$ kg/mol, $M_w / M_n = 1.13$) was dissolved in toluene to form a 2 wt% solution. After filtered using 0.2 µ Millipore filters, this solution was spin coated onto silicon wafers ($1 \times 1$ cm) and then annealed under vacuum at 140 ºC for 2 hours. Resulting PS films were uniform and without pinholes. Film thicknesses were about 120 nm. This solution was also spin coated onto PDMS 9 flat sheets.

PS-coated PDMS lenses were prepared using so-called “spin coating / float-off” method [16]. After rinsed with distilled water, the annealed PS-coated silicon wafers were dipped in a dish containing distilled water. The dipping was performed by slowly steeping the silicon wafers in the water at a small angle. This allowed gradual migration of water to the PS / silicon wafer interface and final detachment and flotation of the PS film without any folding and excessive stretching [17]. The floated PS film was picked up by a PDMS 9 lens supported on a small piece of a silicon wafer. Such PS-coated PDMS lenses were dried at 65 ºC under vacuum (0.01 mbar) for 1 hour.

7.2.1.2. ITO thin layer on PDMS substrates

The ITO layer on glass samples were kindly provided by Philips, Eindhoven, which are the same materials used in Chapter 6. The ITO layers were deposited on treated PDMS 9 lens and sheet substrates in a Leybold sputter system. The PDMS 9 lenses and sheets were placed in an oxygen plasma chamber for 1 min or slightly oxidize the PDMS surfaces. The sputtering target composition was 90 wt% $\text{In}_2\text{O}_3$ mixed with 10 wt% $\text{Sn}_2\text{O}_3$. The sputter power was 600 W. The deposition was performed at room temperature. The deposition rate was 20 nm/min while the substrate carrier was rotated at 10 rpm. The thicknesses of the ITO layer were 13 nm and 23 nm, respectively.

For the experiments with polyester films, 200 µm thick aromatic polyester (Arylite™)
films, provided by Philips, Eindhoven, were used.

7.2.2. Methods
Adhesion experiments were performed with our home-built JKR apparatus. Generally a motor speed of 100 nm/s and a waiting time of 5 s were applied for all measurements unless mentioned otherwise. All samples were measured at least three times.

7.3. Results and discussion

7.3.1. Application of a thin layer of PS
A thin layer of PS was deposited on PDMS 9 lenses and sheets to make a “composite” sample. We studied the adhesion of three different lens-sheet combinations, labelled as Exp. No. 1-3 (Table 7.1). The results of a contact between a PDMS 9 lens and a PS layer spin coated on glass (No. 1) was used as a reference. The values for $K_i^{\text{eff}}$ and $W_i^{\text{eff}}$ values were obtained from the loading curves according to equation 1.4. The value for $G_i^{\text{eff}}$ at each point was calculated using $K_i^{\text{eff}}$ according to equation 1.1 and averaged. All these values are listed in Table 7.1.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Lens Sheet</th>
<th>$K_i^{\text{eff}}$</th>
<th>$W_i^{\text{eff}}$</th>
<th>$G_i^{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PDMS 9 - PS/glass 120 nm</td>
<td>1.90</td>
<td>44.1</td>
<td>43.7</td>
</tr>
<tr>
<td>2</td>
<td>PDMS 9 - PS/PDMS 9 120 nm</td>
<td>0.91</td>
<td>43.1</td>
<td>43.0</td>
</tr>
<tr>
<td>3</td>
<td>PS/PDMS 9 120 nm</td>
<td>0.90</td>
<td>30.4</td>
<td>29.5</td>
</tr>
</tbody>
</table>

Table 7.1. Samples details and results for the loading curve.

$a$ The ± sign indicates the sample standard deviation using 3-5 data points.

$b t_{PS}$, the thickness of the thin PS film deposited on the PDMS 9 lens and sheet substrates.

When a PDMS 9 lens was brought into contact with a PS/PDMS9 sheet (No. 2), the $W_i^{\text{eff}}$ values were basically the same as in the case where a PS/glass sheet (No. 1) was
used, while the $K^{\text{eff}}_i$ value was about a half of the latter and almost equal to the $K^{\text{eff}}_i$ value for the self-adhesion of PDMS 9 samples (Chapter 2). The variation in $K^{\text{eff}}_i$ is expected according to equation 1.2, because the PS/glass sheet is much stiffer compared to PDMS 9, hence deformation mainly occurs in the PDMS sample. When a PS/PDMS9 sheet was used (No. 2), deformation occurs in both samples for the indentation depth of 15 ~ 20 µm used in our experiments. The soft substrate of PDMS 9 appeared not to influence the $W^{\text{eff}}_i$ value measured under the measurement conditions used.

When the lens and sheet sample were both PS/PDMS 9 (No. 3), lower values $W^{\text{eff}}_i$ and $G^{\text{eff}}_i$ were obtained, while the $K^{\text{eff}}_i$ was equal to the case that only one sample was “composite” sample (No. 2). This surprised us in the beginning, because our observation seemed quite different from literature data [18-20], which gave a $W^{\text{eff}}_i$ about two times of the surface energy of the thin layer material. With contact angle measurements, it was found that the surface energy of PS is $\sim 39$ mJ/m$^2$. Therefore a $W^{\text{eff}}_i$ value of $\sim 78$ mJ/m$^2$ was expected, which was much larger than our experimental value of 30.4 mJ/m$^2$.

One of the most likely reasons for such a deviation is bulk viscoelastic losses due to the relatively fast loading/unloading rates we used in our experiments. Such viscoelastic losses were reported to be present for thin layer of polymers coated on PDMS lenses, even a very low loading/unloading rate, $V = -\frac{da}{dt}$, of 10 nm/s [19]. Under our measurement conditions, $V$ was $\sim 500$ nm/s, which was a too fast rate to reach equilibrium. Even for the self-adhesion of PDMS samples, the bulk viscoelastic losses could only be diminished when a $V = 100$ nm/s was used, as was demonstrated in Chapter 4. Therefore, in our experiments, the presence of these non-elastic losses in PS would strongly influence the results unless an extremely slow speed could be applied. Another possible reason, as mentioned in Chapter 6, is the constant $K^{\text{eff}}_i$ values we used in our calculations of using the JKR model (see also Chapter 6). This value is very likely to be non-constant for such a “composite” sample.
Using the $K_i^{\text{eff}}$ values reported in Table 7.1, $G_i^{\text{eff}}$ values were calculated using equation 1.1 and is shown in Figure 7.1. The $t_{\text{delay}}$ data for the contact between different lens-sheet combinations are listed in Table 7.2. These data showed that for PDMS 9–PS/glass (No. 1) and PDMS9–PS/PDMS 9 (No. 2) combinations, the values of $G_i^{\text{eff}}$ and $G_u^{\text{eff}}$ were very similar under the measurement conditions used, giving an adhesion hysteresis ($\Delta G = G_u^{\text{eff}} - G_i^{\text{eff}}$) of ~ 7.5 mJ/m$^2$. As was shown in chapter 6, this hysteresis was mainly attributed to the bulk viscoelastic losses of the PDMS 9 lenses. In agreement with this observation, the values of $t_{\text{delay}}$ were also found to be very similar for both combinations (Table 7.2).

![Figure 7.1. Plot of $G^{\text{eff}}$ as a function of contact radius, $a$, for different combination of lens and sheet samples (No. 1-3). Motor speed: 100 nm/s, waiting 5 s.](image)

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lens–sheet</td>
<td>PDMS 9-PS/glass</td>
<td>PDMS 9-PS/PDMS 9</td>
<td>PS/PDMS 9-PS/PDMS 9</td>
</tr>
<tr>
<td>$t_{\text{delay}}$, s</td>
<td>2.2</td>
<td>2.1</td>
<td>11.8</td>
</tr>
</tbody>
</table>

* All experiments were performed at a motor speed of 100 nm/s and a waiting time of 5 s.

When both lens and sheet were “composite” samples (No. 3), The value of $t_{\text{delay}}$ became much larger. A lower value of $G_i^{\text{eff}}$ and a much higher value of $G_u^{\text{eff}}$ gave a
large adhesion hysteresis. Such values were unrealistic for a contact where only van der Waals interactions are present. This strongly suggests that under our measurement conditions, the energy dissipated in the non-elastic deformation of the contact zone may be so large that equation 1.1 and 1.4 can no longer be used to interpret the data for the contact between two composite samples. Many efforts have been made to analyse the JKR measurements of viscoelastic polymers [20-22]. In these models, the key point is that the parameter of $K_i^{\text{eff}}$ is time-dependant. Therefore additional information about the viscoelastic behaviour of a polymer is required.

As we mentioned earlier, another issue is the heterogeneity of the composite sample, which makes the effective elastic modulus dependant on the indentation depth. This effective value is related to the thickness and mechanical properties of the thin layer.

Based on above discussions, it is clear that several factors must be considered when a thin layer of polymer is deposited on a soft elastic substrate to form a “composite” sample for JKR-type measurements. These factors mainly include the bulk viscoelastic losses, the thickness and mechanical properties of the polymer thin layer. Other factors may also play a role, such as the possible plastic deformation of the polymer layer, the roughness of the polymer layer, and the adhesion between the polymer thin layer and the substrate, etc. In the next section, ITO, an inorganic thin layer, was deposited on PDMS substrates to serve as a model different from the polymer thin layer.

**7.3.2. Application of a thin layer of ITO**

ITO layer with a thickness of 13 nm and 23 nm, respectively, was deposited on PDMS 9 lenses and sheets. The values of $K_i^{\text{eff}}$, $W_i^{\text{eff}}$ and for the average of $G_i^{\text{eff}}$ obtained from the loading curves are listed in Table 7.3. The results of the contact between a PDMS 9 lens and ITO/glass sheet (No. 4) was used as reference data (Figure 7.2).
### Table 7.3. Samples details and results for the loading curve.\(^a\)

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Lens layer/substrate</th>
<th>Sheet layer/substrate</th>
<th>(t_{ITO}) (^b)</th>
<th>(K_{eff}^l)</th>
<th>(W_{eff}^l)</th>
<th>(G^l_{eff})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>PDMS 9 - ITO/glass</td>
<td>ITO</td>
<td>1 (\mu m)</td>
<td>1.80</td>
<td>45.3</td>
<td>45</td>
</tr>
<tr>
<td>5</td>
<td>ITO/PDMS 13 nm PDMS</td>
<td>-</td>
<td>-</td>
<td>0.95</td>
<td>36.0</td>
<td>36</td>
</tr>
<tr>
<td>6</td>
<td>ITO/PDMS 23 nm PDMS</td>
<td>-</td>
<td>-</td>
<td>0.90</td>
<td>36.8</td>
<td>36</td>
</tr>
<tr>
<td>7</td>
<td>ITO/PDMS 13 nm ITO/PDMS</td>
<td>13 nm</td>
<td>0.93</td>
<td>34.4</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>ITO/PDMS 23 nm ITO/PDMS</td>
<td>23 nm</td>
<td>0.79</td>
<td>11.9</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>ITO/PDMS 13 nm Arylite (200 (\mu m))</td>
<td>-</td>
<td>1.72</td>
<td>18.5</td>
<td>18</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) The ± sign indicates the sample standard deviation using 3-5 data points.

\(^b\) \(t_{ITO}\): the thickness of the thin ITO film deposited on the PDMS 9 lens and sheet substrates.

### Table 7.4. Values of \(t_{delay}\) for different lens-sheet combinations\(^*\).

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Lens layer/substrate</th>
<th>Sheet layer/substrate</th>
<th>(t_{ITO})</th>
<th>(t_{ITO})</th>
<th>(t_{delay})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>PDMS 9 - ITO/glass</td>
<td>ITO/glass</td>
<td>1 (\mu m)</td>
<td>-</td>
<td>5.1</td>
</tr>
<tr>
<td>5</td>
<td>ITO/PDMS 13 nm PDMS</td>
<td>-</td>
<td>-</td>
<td>25.6</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>ITO/PDMS 23 nm PDMS</td>
<td>-</td>
<td>-</td>
<td>27.3</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>ITO/PDMS 13 nm ITO/PDMS</td>
<td>13 nm</td>
<td>-</td>
<td>19.0</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>ITO/PDMS 23 nm ITO/PDMS</td>
<td>23 nm</td>
<td>-</td>
<td>26.9</td>
<td></td>
</tr>
</tbody>
</table>

\(^*\) All experiments were performed at a motor speed of 100 nm/s and a waiting time of 5 s.

For the lens-sheet combinations for Exp. No. 4-8 (Table 7.3), the values of \(t_{delay}\) are listed in Table 7.4. The plot of \(G^eff\) as a function of contact radius, \(a\), is shown in Figure 7.3 (No. 5 and No. 6) and Figure 7.4 (No. 7 and No. 8). It was found that \(t_{delay}\) values were in line with the trend found for hysteresis.
First we discuss the contact between an ITO/PDMS 9 lens and a PDMS 9 sheet (No. 5 and 6). Comparing Table 7.3 and Figure 7.3, the variation in the thickness of the ITO layer of the composite lens had no effect on the $K_{l}^{eff}$, $W_{l}^{eff}$ and $G^{eff}$ values within the error of measurement. However, application of such composite lenses, compared to the PDMS 9–ITO/glass (No. 4) which is shown in Figure 7.2, showed a lower value of $W_{l}^{eff}$ and $G_{l}^{eff}$ and a larger hysteresis. The reasons for such findings may include
the bulk viscoelastic losses during deformation, possible plastic deformation possible cracks formation at the interface of ITO layer/PDMS substrate. None of these factors are included in the JKR model (equation 1.1 and 1.4) which was used here. Hence, it is unclear if these differences are realistic or deviated because of the limitations of the JKR model. Apart from the possible effects of the composite sample mentioned above, it is also possible that the difference in surface composition and roughness plays a role. Such a difference may be caused by the different sputter temperature used to prepare these samples.

![Graph](image)

**Figure 7.4.** Plot of $G_{\text{eff}}$ as a function of contact radius, $a$. Lens: ITO/PDMS 9, sheet: ITO/PDMS 9 (No. 7-8), motor speed: 100 nm/s, waiting time 5 s.

When both lens and sheet are “composite” samples (No. 7-8), the difference in $K_i^{\text{eff}}$, $W_i^{\text{eff}}$ and $G^{\text{eff}}$ values were much more clear (Figure 7.4 and Table 7.3). More interestingly, the thickness of the ITO layer did influence the obtained values, with a lower $W_i^{\text{eff}}$ and a larger hysteresis for an ITO layer of 23 nm as compared to the 13 nm thick layer. One possible reason is the difference in effective contact area, which is affected by the surface roughness and mechanical properties of the two materials. A decrease in effective contact area will lead to a decrease in measured $G^{\text{eff}}$ value. In a recent publication, Cho et al. [15] studied the adhesion between an ITO coated PDMS lens, with an ITO thickness of 10 nm, and a self-assembled monolayer of various functional groups on a silicon wafer substrate. They proposed to use a multiplying
factor to correct their relatively low $W_{l}^{\text{eff}}$ values. The multiplying factor was the ratio of the surface modulus to bulk modulus according to them. Whether this approximation can be used is questionable.

We think that factors, such as the viscoelastic and plastic deformation, surface roughness, surface modulus of the layer, layer thickness and its mechanical properties, and possible crack formation at the layer/substrate interface, need to be studied much more systematically to come up with reliable conclusions. This further research is out of the scope of this thesis.

**7.3.3. Contact between an ITO/PDMS 9 lens and an Arylite film**

Finally, in order to study the adhesion between an ITO layer and a commercially attractive polymer film, we measured the contact between an ITO/PDMS 9 lens and an Arylite film (No. 9). The values of $t_{\text{delay}}$ data are listed in Table 7.5 for the experiments at different loading/unloading speed and waiting time. It was found that when the same speed was applied, $t_{\text{delay}}$ can be used to demonstrate the hysteresis. While the loading/unloading speed decreased, the observed $t_{\text{delay}}$ became too large to compare with other $t_{\text{delay}}$ values obtained at a faster speed. Therefore, $t_{\text{delay}}$ values are meaningful only when the measurement conditions are similar. The two speeds applied in our experiments differ by a factor of 5. If we divide the $t_{\text{delay}}$ tested at 20 nm/s by this factor, then we obtain a new value of $1345 \times 1/5 = 269$ s. Interestingly, this new value is comparable with other values tested at 100 nm/s. This again suggests that we can only directly compare the $t_{\text{delay}}$ values when the loading/unloading speed is the same.

The plot of $G_{l}^{\text{eff}}$ as a function of contact radius is shown in Figure 7.5. When tested at different motor speed and waiting time, the values of $G_{l}^{\text{eff}}$ were roughly the same. However, $G_{ul}^{\text{eff}}$ values were different. A lower motor speed and longer waiting time slightly enlarged the hysteresis. This confirms again that identical measurement conditions are important to obtain comparable results.

In the measurements, “composite” lenses with an ITO thickness of 13 nm were used. Again, all the possible reasons discussed in the previous section may contribute and
make the calculated values of $K_{\text{eff}}$, $W_{\text{eff}}$ and $G_{\text{eff}}$ doubtful. A large hysteresis was observed for all cases listed in Table 7.5, showing a significant adhesion promotion for the ITO/Arylite interface. To understand the mechanism for this adhesion promotion, further information about the ITO and Arylite surface is needed. However, this is not addressed in this thesis.

Table 7.5. Values of $t_{\text{delay}}$ for an ITO/PDMS 9 lens and an Arylite film (No. 9) measured at different conditions.

<table>
<thead>
<tr>
<th>Loading/unloading rate, nm/s</th>
<th>Waiting time</th>
<th>$t_{\text{delay}}$, s</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 (larger contact radius)</td>
<td>5 s</td>
<td>186</td>
</tr>
<tr>
<td>100 (smaller contact radius)</td>
<td>5 s</td>
<td>179</td>
</tr>
<tr>
<td>20</td>
<td>5 s</td>
<td>1345</td>
</tr>
<tr>
<td>100</td>
<td>15 min</td>
<td>199</td>
</tr>
</tbody>
</table>

Figure 7.5. Plot of $G_{\text{eff}}$ as a function of contact radius, $a$.

Lens: ITO/PDMS 9, sheet: Arylite (No. 9).

7.4. Conclusions

Thin layers of PS and ITO were deposited on PDMS lens and sheet to make a “composite” sample, in order to investigate the influence of thin layers on adhesion behaviour in the JKR measurements.

A useful semi-quantitative comparison can be made by using the JKR model as long as
only one of the samples is coated with a thin layer. When both samples are coated, this model no longer holds. Further study is needed to better understand the possible factors which influence the calculated data, such as the bulk viscoelastic and plastic deformation, surface roughness, layer thickness and its mechanical properties, and possible crack formation during contact at the layer/substrate interface. The values of $t_{\text{delay}}$ and $G^{\text{eff}}$ may be used to demonstrate the hysteresis. Measurement conditions strongly influence these values and attention must be paid when comparisons are made between these data.

References

Elastic moduli of poly(butyl acrylate)-based rubbery coatings measured by micro-indentation

8.1. Introduction

In chapter 3 we have shown that the micro-indentation technique can be used as a reliable and convenient tool for an accurate estimation of the elastic modulus of a rubber-like sheet and coating on a substrate. As described in chapter 3, the elastic modulus and hardness can be determined on the basis of the experimental data from the indentation load, \( P \), and displacement, \( h \) [1]. Based on the \( P-h \) curve, the tip-sample reduced modulus \( E_r \) is calculated using the following equation:

\[
E_r = \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}} \tag{8.1}
\]

where \( A \) is the contact area at full load, \( S \) is the unloading stiffness, and \( \beta \) is the geometry constant, equal to 1.034 for a Berkovich indenter. The reduced modulus is related to the elastic modulus of the material being tested by

\[
\frac{1}{E_r} = \frac{1}{E} + \frac{1}{E_i} - \frac{1}{1 - \nu^2} \tag{8.2}
\]

where \( E \) and \( \nu \) are the elastic modulus and Poisson’s ratio for the material, respectively, and \( E_i \) and \( \nu_i \) are the same parameters for the indenter. For a diamond indenter, as is used here, the values of \( E_i \) and \( \nu_i \) are 1141 GPa and 0.07, respectively [2]. For perfect rubbery materials, the Poisson’s ratio is taken as 0.5.

In the past decade the micro- and nano-indentation techniques have been used for probing mechanical properties of polymer coatings/films [3-11]. However, the application of this technique to determine these properties for soft or compliant materials is limited. A major impediment to the use of this technique in characterizing compliant polymeric or biological materials is the often time-dependent response (creep on fixed load, stress-relaxation on fixed displacement), leading to ambiguity in interpretation of \( P-h \) curves [7]. A consequence of pure elastic contact is that the
contact size or indenter displacement will decrease spontaneously as load decreases. When viscosity effects dominate, however, the indenter displacement can actually increase first for a short time, even though the load has started to decrease from the full load at the onset of unload. The resultant load-displacement plot in this case will exhibit a “nose” in the unloading segment [4]. This may lead to an overestimation of the contact stiffness and hence the recuded modulus of the sample. Several models have been proposed to correct these viscoelastic effects by modeling the unloading contact stiffness [4, 7, 12].

For perfect rubbery materials, no such “nose” behavior is expected because the response is purely elastic. This is indeed what we observed in the micro-indentation results of crosslinked PDMS materials (see Chapter 3). However, in the literature, quite often some hysteresis was found between the loading and unloading curve, indicating viscoelastic effects in the testing material [8, 10-11]. Therefore, to determine the actual elastic modulus of a real rubbery coating using equation 8.1 and 8.2 may be a problem. The modulus values found may be influenced by the materials properties and the contact conditions, such as geometry of the contact, penetration depth, the loading/unloading rate and the ambient temperature [3].

This chapter investigated the (visco)elastic response, during micro-indentation, of crosslinked coatings prepared from a telechelic carboxyl-terminated poly(butyl acrylate) with a narrow molecular weight distribution and a random co-polymers on average the same functionality and molecular weight. These measurements were used to determine the elastic moduli of these crosslinked coatings. Particular attention is given to the influence of the dangling chains on the moduli values of coatings prepared from telechelic polymers.

8.2. Experimental

8.2.1. Materials
Telechelic carboxyl-terminated poly(butyl acrylate), random poly (acrylic-acid-co-butyl acrylate) and mono-functional polymer (with one carboxyl group per chain) were synthesized and characterized according to the procedure described elsewhere [13]. The $M_n$, $MWD$ and COOH-group functionalities are listed in Table 8.1

The crosslinker triglycidyl isocyanurate (TGIC), with an epoxy functionality of three,
was used as received (Aldrich, 98%).

The catalyst 1,4-diazabicyclo[2.2.2]octane (DABCO) (98+%, Merck) was used as received. Acetonitrile (HPLC grade, 99+%, Biosolve) was used as the solvent.

**Table 8.1.** $M_n$, MWD and COOH-group functionalities, and the glass transition temperature ($T_g$) of the three starting polymers

<table>
<thead>
<tr>
<th></th>
<th>$M_n$, g/mol</th>
<th>MWD</th>
<th>COOH functionality per chain on average</th>
<th>$T_g$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Techelic polymer</td>
<td>2100</td>
<td>1.13</td>
<td>1.985</td>
<td>- 61.2</td>
</tr>
<tr>
<td>Random copolymer</td>
<td>2200</td>
<td>1.75</td>
<td>2</td>
<td>- 46.9</td>
</tr>
<tr>
<td>Mono-functional polymer</td>
<td>2300</td>
<td>1.14</td>
<td>1</td>
<td>-</td>
</tr>
</tbody>
</table>

**8.2.2. Sample preparation**

In general, the coatings used in our experiments were made from mixtures of polymer – TGIC – DABCO using the following ratios:

- [epoxy] : [COOH] = 1.0 : 1 ~ 2.0 : 1 (molar ratio)
- [epoxy] : [DABCO] = 1 : 0.07 (weight ratio)

A variation in the [epoxy] : [COOH] ratio (1.0 ~ 2.0) was employed. The ratios of [epoxy] : [COOH] are expressed assuming a 100% purity and a functionality of 3 for TGIC.

Mono-functional polymer was added to the mixtures of telechelic polymer – TGIC – DABCO polymer to prepare crosslinked networks with dangling chains. The weight percentages of mono-functional polymer to the total weight of polymers were 5 wt %, 10 wt % and 20 wt %. When mono-functional polymer was used, the [epoxy] : [COOH] ratio was always kept at 1.6 : 1.
The polymer, the cross-linker and the catalyst were initially dissolved in acetonitrile (50 wt %) and applied on an aluminum substrate. All plates were placed under a ventilated fume hood for 30 min, in order to evaporate some of the solvent and avoid crater formation during the cure. The aluminum plates were then placed overnight in an oven at 120°C for crosslinking to occur. The thickness of the coatings after cure was 100 ~ 120 µm. Samples were cut into 1 × 1 cm for the micro-indentation measurements.

8.2.3. Methods
Micro-indentation experiments were conducted in air at room temperature, with a loading rate of 40 nm/s. The load applied was in the range of 1 ~ 2 mN. Samples were measured for 3 times at each load.

8.3. Results and discussions
8.3.1. Effect of the indentation depth
Before we compare the calculated elastic moduli based on the micro-indentation experiments, a safe indentation depth without seeing the effect of the aluminum substrate needs to be found. In chapter 3, we proved the validity of the 10% rule [14] on our crosslinked PDMS coatings on polycarbonate substrates. To see whether this rule also holds for the coatings discussed here, the $E_r$ values were measured with different indentation depths.

The $E_r$ values as a function of the ratio of indentation depth to the total thickness of the coating ($h/h_t$) are shown in Figure 8.1 for coatings prepared from telechelic polymer ($a$) and random polymer ($b$). The $E_r$ values measured within the error of measurements are not influenced by the substrate for our crosslinked coatings when the indentation depth ($h$) is less than about 15 % of the total thickness of the coating ($h_t$). This observation is generally in line with the 10 % rule which we found for our crosslinked PDMS coatings (Chapter 3). Therefore, indentation results presented in the following sections of this chapter were based on the shallow indentation experiments with an $h/h_t$ ratio less than 0.15.
Figure 8.1. Evolution of $E_r$ versus $h/h_t$ ratio for the crosslinked coatings prepared from (a) telechelic polymer and (b) random co-polymer. [epoxy] : [COOH] =1.4 :1.

8.3.2. Effect of [epoxy] : [COOH] ratios

The $E_r$ values for the crosslinked telechelic polymer-based and random polymer-based networks prepared with different [epoxy] : [COOH] ratios are shown in Figure 8.2. The effect of the [epoxy] : [COOH] ratio on this mechanical property appears to be large. The $E_r$ values increase with increasing the amount of epoxy functions present in the formulation before cross-linking.
Figure 8.2. Evolution of $E_r$ for crosslinked poly(butyl acrylate) networks with different [epoxy] : [COOH] ratios. Loading force = 1 mN.

According to rubber elasticity theory [15-17], the elastic modulus is related to the molar mass between chemical crosslinks ($M_c$) as the following equation:

$$E = \frac{3\rho RT}{M_c}$$

(8.3)

where $\rho$ is the density of the poly(butyl acrylate) network, $R$ the gas constant and $T$ the absolute temperature. This formula is valid well-above $T_g$. The $T_g$ of our networks was experimentally determined by DSC and are in the range of -8.5 ~ -30 °C [13a]. Performing the micro-indentation experiments at room temperature, we may assume that rubber elasticity theory is applicable to our coatings. It is generally assumed that a minimum of 20 monomer units in the polymer chain is needed for the rubber elasticity theory to be applicable. We are with our systems a little bit below this limit, however, we still consider that comparing our experimental results to the theoretical ones is relevant and the possibility of physical crosslinking can be neglected.

Assuming that $M_c$ is equal to the molar mass of the telechelic polymer, $M_n (= 2000$ g/mol), and a value of 1 g/ml for the density of the network, a theoretical value for the elastic modulus, $E$, of 3.7 MPa can be calculated using equation 8.3. From this value, and assuming a Poisson’s ratio of 0.5, we calculated a theoretical $E_r$ value of 4.9 MPa. This theoretical value is close to the value observed for [epoxy] : [COOH] ratios of
1.4, 1.6 and 2. Hence, the most “perfect” network is probably formed with an \([\text{epoxy}] : [\text{COOH}]\) ratio of 1.4 ~ 2.0 which is higher than 1:1. The \(E_r\) values measured for \([\text{epoxy}] : [\text{COOH}]\) ratios of 1 and 1.2 are much lower than the one predicted by the rubber elasticity theory. This can be explained by incomplete crosslinking reaction between the epoxy and acid groups. The impurities in the cross-linker also lower the actual amount of epoxy groups in the formulation, and lower the actual \([\text{epoxy}] : [\text{COOH}]\) ratios.

A steep increase in \(E_r\) with an increase in \([\text{epoxy}] : [\text{COOH}]\) ratio was observed in Figure 8.2. If we take the network prepared with \([\text{epoxy}] : [\text{COOH}] = 1.6 : 1\) as the “perfect” network and \([\text{epoxy}] : [\text{COOH}] = 1.0 : 1\) as the most “imperfect” network, a comparison of \(M_c\) calculated using equation 8.3 can be made as:

\[
\frac{M_c(1:1)}{M_c(1.6:1)} = \frac{E_r(1.6:1)}{E_r(1:1)}
\]

This leads to a ratio of 2.4 ± 20 %. The ratio of \(M_c(1:1) / M_c(1.6:1)\) obtained from solid state NMR \(T_2\)-relaxation time measurements give a value of 2.8 ± 10 % [13a], confirming the value calculated from our moduli data.

For the \(E_r\) of the random copolymers-based networks, we observed a trend similar to the one of the telechelic polymers-based networks, but the \(E_r\) values of random copolymers-based networks are always lower. A main factor explaining these lower values may be the incomplete crosslinking reactions. Another factor explaining this lowering might be the different number and positions of \(\text{–COOH}\) groups of each chain. Chromatographic characterization of the starting random copolymer showed that the number of acid groups along the chain was between 0 and 6 [13b]. This will lead to a large number of network defects, such as nonreacted and dangling chains and a wide variation in \(M_c\). These factors are possibly responsible for the lower \(E_r\) values and larger hysteresis found for random polymer-based coatings. The hysteresis phenomena will be discussed in next section.

### 8.3.3. The hysteresis for a loading and unloading cycle

As mentioned in the previous section, the (almost) “perfect” network is obtained with an \([\text{epoxy}] : [\text{COOH}]\) ratio of 1.4 ~ 2.0, using the telechelic polymer as the starting polymer. The \(P-h\) curves of coatings prepared from telechelic and random polymers with \([\text{epoxy}] : [\text{COOH}]\) ratios in this range are shown in Figure 8.2. The \(T_g\) of all
crosslinked poly(butyl acrylate) coatings tested in this chapter were found to be below room temperature, in the range of -8.5 ~ -30 °C [13]. Therefore, we expect a $P-h$ curve for these rubbery materials very similar to those we observed in Chapter 3. However, hysteresis between the loading and unloading curves was always observed for all coatings tested here, whereas for crosslinked PDMS materials presented in Chapter 3, no hysteresis was found when the same speed and same load were applied. We believe that this hysteresis is caused by the bulk viscoelasticity of the sample itself.

**Figure 8.3.** $P$ versus $h$ for (a) crosslinked telechelic polymer-based and (b) random polymer-based poly(butyl acrylate) networks.
It is interesting to notice that such hysteresis for telechelic polymer-based coatings (Figure 8.3a) is much less than for random polymer-based coatings (Figure 8.3b). As stated above, the hysteresis is an indication of bulk viscoelasticity of the material; hence this observation shows that crosslinked random polymer-based coatings are more viscoelastic than the telechelic polymer-based coatings. We can explain this by the difference in the starting polymer used for crosslinking. For telechelic polymers, each polymer has two –COOH groups at the chain ends. After crosslinking with an optimum [epoxy] : [COOH] ratio (1.4 ~ 2.0), the obtained network has a well-controlled structure and can be regarded as a “perfect” network. For random copolymers, the number and position of –COOH groups of each chain was not controlled and different from chain to chain, therefore the obtained networks may contain a large number of network defects, such as nonreacted chains and dangling chains and a larger variation in \(M_c\). Such defects are likely to be responsible for the larger hysteresis observed in Figure 8.3b. It seems that the hysteresis observed in the \(P-h\) curves can be used to get information about the perfectness of a crosslinked coating.

According to Ngan and Tang [4], the hysteresis they observed could be lowered by lowering the applied load or the unloading rate. This cannot be the explanation for the difference observed in Figure 8.3a and Figure 8.3b, because the applied load and unloading rate are very similar in our measurements.

### 8.3.4. Influence of dangling chains

**Figure 8.4.** The \(E_r\) values of crosslinked telechelic polymer-based networks prepared with various amounts of mono-functional polymer ([epoxy] : [COOH] = 1.6 : 1). The solid line serves to guide the eye only.
As shown in Figure 8.4, the $E_r$ decreases continuously with an increasing amount of mono-functional polymer added to the telechelic coating formulation. This observation is in line with our results presented in Chapter 4 where dangling chains were introduced to the crosslinked PDMS networks. The more mono-functional polymer added to the telechelic coating formulation, the more dangling chains are present in the crosslinked networks. According to equation 8.3, the $M_c$ value increases when increasing the amount of dangling chains.

It is known that for crosslinked coatings, the glass transition temperature and the elastic modulus can both be described as a function of the molecular weight between crosslinks [18]. As shown in previous work [13a] and Figure 8.5, a linear relation was found between the $E_r$ and $T_g$ for the telechelic polymer-based coatings with and without the addition of dangling chains. This observation confirmed that both $T_g$ and the elastic moduli of our telechelic polymer-based coatings are linearly related to the $M_c$ values of the coatings.

The addition of dangling chains to the telechelic coating formulation brought hardly any change on the $P-h$ curves compared to those of telechelic polymer-based coatings with no dangling chains. An example with the addition of 10 wt % mono-functional polymer is given in Figure 8.6. A small hysteresis was observed between the loading and unloading curves. Compared to Figure 8.3, it is reasonable to conclude that the
main contribution to the larger hysteresis observed for the random copolymer-based coatings (Figure 8.3b) is the larger variation in $M_c$ of the coating. Dangling chains appeared hardly to influence the hysteresis. Hence, micro-indentation measurements may also give information about the variation in distance between crosslinks of rubbery coatings.

**Figure 8.6.** $P$ versus $h$ of crosslinked telechelic polymer-based network with the addition of 10% mono-functional polymer.

### 8.4. Conclusions

We have used the micro-indentation technique to measure the elastic moduli of crosslinked poly(butyl acrylate) coatings at micro-penetration depth. No effect of substrate was found when the indentation depth is less than about 15% of the total thickness of the coating.

We compared the calculated $E_r$ of crosslinked coatings prepared from linear telechelic polymers and linear random polymers with on average the same functionality and $M_n$ values. The $E_r$ values increased with an increase in [epoxy] : [COOH] ratio. Compared to the random copolymer-based coatings, telechelic polymer-based coatings were found to have higher $E_r$ values, when the same [epoxy] : [COOH] ratio was used to prepare the coatings. The influence of the dangling chains on the $E_r$ values of the telechelic polymer-based coatings was demonstrated by employing various amounts of well-defined mono-functional polymer in the telechelic polymer
formulation before crosslinking. $E_i$ values decreases with an increasing amount of dangling chains.

A hysteresis between the loading and unloading curves was observed for both telechelic polymer-based and random copolymer-based coatings, indicating the effect of bulk viscoelasticity of the coating itself. The hysteresis found for telechelic polymer-based coatings was much less than for random copolymer-based coatings. The $P-h$ curves hardly show any difference with and without the addition of dangling chains to the telechelic polymer-based coatings. This suggests that the relatively large hysteresis found in the indentation measurements of the random copolymer-based coatings may be explained mainly by the larger variation in $M_c$ of the crosslinked coatings.

References


Chapter 9

Conclusions and recommendations

9.1. Conclusions

The mesoscopic adhesion on crosslinked PDMS-based materials is in-depth investigated in this thesis, with a focus on the adhesion and adhesion hysteresis under non-equilibrium conditions. A newly built JKR apparatus is used, together with other techniques such as contact angle and micro-indentation measurements, to determine the adhesion properties as well as the (surface) mechanical properties of materials studied. Other techniques, Special attention is given to the self-adhesion of crosslinked PDMS, and to the influence of the presence of submicrometer fillers, surface modification and the deposited thin top layers on adhesion. The latter subjects are related to practical adhesion problems.

A brief introduction about adhesion, adhesion measurement techniques, materials used in our study as well as the outline of this thesis was given in the Chapter 1.

The reliability of our home-built JKR apparatus was confirmed by comparing the self-adhesion results of our crosslinked PDMS materials with literature data and with results determined by contact angle measurements and micro-indentation (Chapter 2).

The self-adhesion of crosslinked PDMS was studied in more detail in Chapter 4. All samples showed constant values of strain energy release rate, $G^\text{eff}$, for the loading part of the JKR curves. The observed adhesion hysteresis for “perfect” crosslinked PDMS materials measured at a normal motor speed (200 nm/s) is attributed to the bulk viscoelastic losses, which can be diminished when a much lower motor speed is applied. The introduction of dangling chains increased the adhesion hysteresis. The presence of a sol fraction at the interface can mask the observed hysteresis, while the extraction of a sol fraction increases the hysteresis if other factors apart from bulk viscoelastic losses contribute to the hysteresis. We found that the observed hysteresis strongly appeared to be related to the elastic modulus of our crosslinked PDMS materials and to the average molar mass between crosslinks, $M_c$, of the extracted
crosslinked PDMS. This may be explained by the interpenetration and entanglement of the surface chains. This chain interpenetration seems to be kinetically controlled by the $M_c$ values of both materials.

In Chapter 5 PDMS-based inorganic/organic hybrid materials containing in-situ precipitated SiO$_2$ were studied. The sample surfaces made in contact with air had a silica-free PDMS top layer of ~ 2 nm thick. For the surfaces made in contact with different substrates (Si-, PS- and Al- surfaces), SiO$_2$ are more likely located at or beneath the outermost atomic layer, and polar –OH groups at the surface of SiO$_2$ can easily stretch out to the outermost atomic layer forming hydrogen bonding at the interface. This difference in surface structure was found to influence the adhesion properties strongly when contacting an unfilled PDMS lens. The JKR technique probes the adhesion and interfacial properties between two solid materials with a larger penetration depth compared to contact angle measurements which only probe the adhesion at the surface.

The surface of a crosslinked PDMS lens contains polar groups such as –OH groups and becomes smoother after treatment with UV/O$_3$. The adhesion between treated PDMS lenses and flat sheets of PDMS 9, polystyrene (PS) and indium tin oxide (ITO) was investigated using the JKR model. The treatment time was found to influence the both the loading and unloading results. Factors such as the non-elasticity and heterogeneity of the oxidized lens in the deformation zone and the roughness of the sheet sample may cause deviations when the JKR model is directly used. After the PDMS lens was treated with UV/O$_3$, adhesion appeared to be promoted for the sheet of PDMS 9 and ITO, especially a longer waiting time is applied, although the increase in lower when the treatment time is longer. Almost no adhesion promotion was observed for the contact between a treated PDMS lens and a PS sheet (Chapter 6).

In the work presented in Chapter 7 an organic thin layer of polystyrene (PS) and an inorganic thin layer of indium tin oxide (ITO) were deposited on crosslinked PDMS lenses and sheets to make “composite” samples for the adhesion study. Semi-quantitive comparison can be made by using the JKR model as long as only one of the samples is coated with a thin layer. Attention must be paid when analysing the results using the JKR model, if both samples are coated with a thin layer. Further study is needed to better understand the possible factors which influence the calculated data, such as the bulk viscoelastic and plastic deformation, surface roughness, layer thickness and its mechanical properties, and possible crack formation.
during contact at the layer/substrate interface.

As a comparing method, the elastic modulus of a rubbery coating was determined using the micro-indentation for crosslinked PDMS (Chapter 3) and for crosslinked carboxyl-terminated poly(butyl acrylate) (Chapter 8). The micro-indentation technique can be used as a reliable and convenient tool for an estimation of the elastic modulus of a rubbery coating.

9.2. Recommendations

In this thesis, the JKR technique has been demonstrated to be a successful method to determine adhesion as well as the elastic modulus of crosslinked PDMS. For crosslinked PDMS with a $T_g$ far below room temperature, under our experimental conditions, the influence of bulk viscoelastic losses was still present, but could be reduced using a much lower loading/unloading rate. Such an influence may be much more obvious for a more complicated system such as crosslinked PDMS containing fillers, surface modified PDMS and PDMS coated with a thin top layer. A detailed comparison between experiments with varying loading/unloading rate will be helpful.

Our research focused on the adhesion measurements under non-equilibrium conditions, which means the total time of contact was relatively short. Although our work is more comparable with more practical situations, a study of adhesion in the equilibrium state is also of great importance in understanding the adhesion behavior between solids. To do so, a much longer time of contact is required. Our JKR apparatus appeared to be very useful in performing quick measurements. Also this apparatus was constructed to be precise in obtaining good contact images, which lowers the error in determining the contact radius. However, for measurements under equilibrium, this apparatus needs to be modified because of the drift of force data.

The application of the JKR technique on other commercially attractive coating/substrate and new materials is likely to be the field of interest in the adhesion area. Crosslinked PDMS is a suitable substrate for such purposes, because either organic or inorganic layers can be easily deposited on the surface of PDMS. However, care must be given in preparing such “composite” samples and interpreting the experimental data.
MESOSCOPIC ADHESION OF POLY(DIMETHYLSILOXANE)

— Self-adhesion, Effects of Fillers, Surface Modification and Thin Top Layers

Summary

The objectives of this project are (1) the design and construction of the JKR apparatus and testing of the reliability of this apparatus; (2) the study on the factors which affect the adhesion behavior of self-adhesion of crosslinked PDMS materials; (3) the study, based on crosslinked PDMS materials, on the influences of submicrometer fillers, surface modification and thin top layers on the adhesion properties.

This thesis mainly contains two parts. The first part, including Chapter 2 and Chapter 4, focuses on the self-adhesion of crosslinked PDMS. The reliability of our home-built JKR apparatus in the adhesion study was confirmed. Based on this, the influence of several factors on the self-adhesion and adhesion hysteresis of crosslinked PDMS were investigated, such as molecular weight of the starting linear PDMS polymers, the bulk viscoelasticity, the sol fraction, the surface roughness, dangling chains, the use of crosslinker in excess and the average molecular weight between crosslinks. The influence of bulk viscoelastic losses can be diminished when lowering the loading/unloading rate. Sol factions were found to mask the observed hysteresis. The network structure was related to the observed hysteresis by the average molar mass between crosslinks, $M_c$.

Based on the build-up knowledge on self-adhesion study on crosslinked PDMS, another important part, including Chapter 5, Chapter 6 and Chapter 7, addressed the adhesion study using the JKR technique towards a more practical direction. Chapter 5 focused on the study on the influence of submicrometer SiO$_2$ particle present at or close to the surface on the adhesion properties of crosslinked PDMS materials. Two types of surfaces are prepared for study: surfaces made in contact with air and made in contact with silicon wafers. A comparison between the differences measured by JKR and CA was made. The JKR measurements probe the adhesion and interfacial properties between two solid materials with a larger penetration depth than that of contact angle measurements.
In Chapter 6, adhesion between a UV/O₃ treated PDMS lens and a sheet of non-treated PDMS, polystyrene (PS) and indium tin oxide (ITO) was investigated using the JKR model. The treatment time was found to influence the both the loading and unloading results. The applicability of the JKR model was discussed. Adhesion appeared to be promoted obviously for the PDMS and ITO, but not for PS, especially a longer waiting time is applied. Longer treatment time was found to decreases the adhesion promotion.

Extension of the JKR technique to other commercially attractive coating/substrate systems was discussed in Chapter 7. An organic thin layer of polystyrene (PS) and an inorganic thin layer of indium tin oxide (ITO) were applied on the surface of crosslinked PDMS lenses. At least semi-qualitative results on the adhesion properties of such materials were obtained from the JKR measurements. Care must be given for interpreting and comparing the calculated results directly using the JKR model, while this model is not applicable.

As an additional part of this thesis, the application of the micro-indentation for determining the elastic modulus of a rubbery coating are presented in Chapter 3 for crosslinked PDMS and Chapter 8 for crosslinked carboxyl-terminated poly(butyl acrylate). The micro-indentation technique was found to be a reliable and convenient tool for an estimation of the elastic modulus of a rubbery coating.
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Curriculum Vitae

Zhili Li was born on the 6th of July 1973 in Sichuan province, P. R. China. In 1992, she graduated from high school and started studies at the Sichuan University, China. She obtained her B.Sc. degree in Polymer Materials Science and Engineering in June 1996 and M.Sc. degree in Polymer Materials in June 1999. After graduation, she had worked in industry companies for three years. In June 2002, she joined the group of Polymer Technology, and moved in December 2002, as a Ph.D. student, to the group of Materials and Interface Chemistry within the Department of Chemical Engineering and Chemistry at Eindhoven University of Technology in The Netherlands. The results of her research, under the supervision of prof.dr. G. de With, dr. J.C.M. Brokken-Zijp and dr.ir. L.J.M.G. Dortmans, have resulted in this thesis.