Non-Contact Rolling Bond Stiffness Characterization of Polyvinylpyrrolidone (PVP) Particles

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Abstract
Two techniques, based on a contact lateral pushing and a noncontact base excitation, were utilized to characterize the adhesion behavior of polyvinylpyrrolidone (PVP) particles. The micro-spherical PVP particles deposited on silicon substrates were excited by an ultrasonic transducer and the transient particle response was acquired by an interferometer. The natural frequencies of the particle rocking motion were extracted by comparing the vibrational spectra of the particles to those of the substrate. The obtained frequencies were then used to determine the work of adhesion of the contact. Rolling resistance moment-based lateral pushing experiments were also conducted on similar PVP particles. The resulting slopes of force–displacement curves were utilized to obtain the work of adhesion. The work of adhesion results determined from the noncontact measurements and lateral pushing measurements were in good agreement. In order to characterize the particle/substrate adhesion bond, different contact modes (i.e., rigid contact, neck-shaped contact, and an equivalent torsional spring) in the contact area were considered. For each case, the expected natural frequencies of the rocking motion were extracted from the slopes of force–displacement curves obtained in the contact lateral pushing experiments. The existence of all possible modes of the particle/substrate bond was verified because all expected natural frequencies were observed in the noncontact acoustic measurements.

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Keywords
Work of adhesion, micro-spherical particles, polyvinylpyrrolidone (PVP) adhesion characterization, base excitation approach, contact rolling approach, torsional stiffness of the bond

1. Introduction

Compared to various other types of forces such as inertia, gravity, and electrostatic, adhesion (weak intermolecular interaction or van der Waals force) can be a dominant force at the micrometer length scale. Accurate adhesion characterization of micro-scale objects (e.g., micro-particles, micro-machined moving parts, micro-electronic components, and biological cells) is, therefore, essential for various in-

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dustries such as pharmaceuticals, printing/copying, MEMS (microelectromechanical systems), medical devices, and semiconductor manufacturing. In pharmaceutical industry, during the processing and handling of powder, powder particles come in contact with several surfaces. During such contact, van der Waals force is typically dominant and may cause the powder particles to adhere to these surfaces, resulting in a loss of material from the formulation and a substantial alteration of its flowability. For low dose drugs, interactive mixtures of drug powder and an excipient material are often used to improve the homogeneity of the powder mixtures. In an interactive mixture, the drug particles are considered to firmly adhere to the carrier particles [1]. However, low adhesion between the drug particles and the surfaces of mixers, storage containers or hoppers would be desirable since drug particles are not pulled off from the excipient particles when they are in contact with these surfaces during handling and manufacturing. In practice, if the adhesion properties of the powder particles attached to surfaces are known, and drug–excipient and excipient–excipient adhesion strength is understood, the most suitable material can be chosen and/or their properties can be modified.

In the current study, a noncontact technique based on acoustic base excitation and laser interferometry [2, 3] was used to characterize the adhesion properties between a commonly used round-shaped tablet binder, polyvinylpyrrolidone (PVP), and a silicon surface. Even though PVP samples used included deformed particles due to particle-to-particle and particle-to-surface contacts, round PVP particles can be produced using the current nucleation-based chemical processes. The surface energy of silicon is well known and its surface quality (e.g., flatness) can be well controlled. Therefore, the work of adhesion determined in this study can be used to investigate the interactions of the PVP particles with other types of surfaces. In the noncontact technique, the difference in phase between a scattered/reflected light from a particle (top) surface and the reference beam is measured, and this phase difference is proportional to the instantaneous surface displacement [4]. The natural frequencies of the particle–substrate bond in different modes of motion were related to the work of adhesion between the particle and the substrate. It is noteworthy that during the experiments the spherical particles are not dislodged from their contact zones. The determined work of adhesion data were compared with those obtained from rolling resistance moment-based lateral pushing experiments for similar particle–substrate system.

Accurate measurement of adhesion force at micro/nano-scale and relating it to the work of adhesion of the particle–substrate system is often a challenging task due to the small length-scale and the low force levels involved. Currently, adhesion forces are often characterized either by measuring the force required for adhering a particle to a surface or for detaching a particle from a surface [1]. Advanced techniques (e.g., force microscopy) are needed for measuring the adhesion properties during adhesion phase, while commonly-used techniques mostly measure adhesion properties during detachment. Some of the commonly-used methods include centrifuge technique, aerodynamic method, hydrodynamic technique [5], impact-
spectrum method, and ultrasonic vibration method [6]. In the centrifuge technique, the centrifugal force required for detaching a particle from the substrate while the substrate is in rotation is measured. In the aerodynamic and hydrodynamic techniques, the flow-generated force is used to detach a particle from the substrate, and the threshold force is used to determine the force of adhesion. Whereas in the impact-spectrum technique, a number of particles are detached from a substrate by the impact given at the opposite sides of the substrate and the adhesion force is measured. In the ultrasonic vibration method, the frequency and hence the force required to detach a particle from the substrate using an ultrasonic probe is measured. In [7], a device setup developed for determining the adhesion bond stiffness between a particle and a substrate from the natural frequency shift of the oscillatory system is presented.

The force microscopy techniques that measure the adhesion force during the formation of adhesion bonds include atomic force microscopy (AFM) [8–12], lateral/friction force microscopy (FFM) [13, 14], scanning tunneling microscopy (STM), and ultra-high vacuum atomic force microscopy (UHV-AFM) [15, 16]. In most of these techniques, a cantilever tip is brought near a particle on a surface whose properties are to be measured. The deflection in the cantilever due to the adhesion force is measured. All the above-specified force microscopy methods need some form of contact between the cantilever and the particle/surface except the STM, which is a noncontact method. In the STM method the electric current between the tip and the particle/surface is measured, which is proportional to the adhesion force.

In the pharmaceutical research, AFM [17] and centrifuge techniques [18] are widely used for particle–substrate adhesion characterization of active pharmaceutical ingredients (APIs) and excipients in order to determine their adhesion properties. AFM is a contact method. In the AFM-based adhesion studies, the particle is brought into contact with and separated from a substrate. The maximum force needed to detach the particle from the substrate is measured and the particle–substrate adhesion is evaluated. In such measurements, the AFM tip–object interactions are highly nonlinear and complex due to gluing of the probe tip to the object (particle) and, also, the technique attempts to characterize the properties of a single contact (particle–surface) by creating two contact points (particle–surface and particle–probe tip). Since the particle has to be glued to the tip of a probe, it is essentially a destructive technique. Centrifuge technique is a noncontact method, which measures the centrifugal force required for detaching a particle from the substrate while the substrate is in rotation. This technique provides statistical data for a large number of particles.

In the current work, two different techniques, based on contact lateral pushing and noncontact acoustic base excitation experiments, were utilized to characterize the adhesion properties of PVP particles on flat substrates. The main advantage of using a laser interferometer (in base excitation experiments) in adhesion measurement is the ability to measure surface displacements down to couple of nanometers
at high vibration frequencies in a noncontact manner. As a result, the resonance frequency of such a motion can be related to the work of adhesion of the particle–substrate bond without contacting and altering the surface of the particle. The resulting work of adhesion determination technique is noncontact and non-destructive. On the other hand, determining the onset of rolling and the critical rotation angle is not feasible with the current base excitation setup. In order to find the critical rotation angle and pre-rolling and rolling stiffness of the particle–substrate adhesion bond, a lateral contact pushing experiment needs to be conducted as well. The work of adhesion can then be determined based on the obtained pre-rolling stiffness of the particle–substrate adhesion bond and be compared to the results from the noncontact acoustic base excitation tests.

2. Materials

During tablet manufacturing, essential excipients associated with sticking problems are binders and lubricants. The typical binder, PVP, which is water-soluble and obtained by radical polymerization of N-vinylpyrrolidone, has been known for its effective ability to modify adhesion properties [19]. PVP is one of the most commonly used biomaterials in pharmaceutical formulations. In the current study, PVP microparticles (Kollidon® 30, BASF Corporation, Rhineland-Palatinate, Germany) with a particle size of 20–60 µm were employed for adhesion characterization. PVP is regarded as a non-toxic synthetic polymer because it is not absorbed through the gastrointestinal tract or mucous membranes. Furthermore, it does not cause any irritation or sensitization effect on the skin. Based on these acceptable properties for pharmaceutical applications, PVP has found wide application as a disintegrant, suspending agent, coating agent, tablet binder, and hydrophilizing biomaterial [19]. Because of the popularity of PVP in pharmaceutical processing, its surface adhesion characteristics affect numerous pharmaceutical unit operations such as granulation, blending, lubrication and compaction.

Although PVP particles have various shapes (Fig. 1), only spherical particles were chosen for this study because, compared to irregularly-shaped ones, the contact shape and adhesion properties of such particles are better understood. The behavior of non-spherical particles is beyond the scope of this study. Scanning electron microscope (SEM) images of individual PVP particles as well as groups of particles are shown in Fig. 1. The actual diameters of the individual PVP particles used in the experiments were determined by digital processing of optical microscope images. The PVP particles were dry-deposited onto a plasma cleaned single-crystal silicon substrate (p-type doped (100) oriented wafer) immediately prior to the measurements. The mass density ($\rho_1$), Young’s modulus ($E_1$), and Poisson’s ratio ($\nu_1$) of the PVP particles were estimated as $\rho_1 = 1210$ kg/m$^3$, $E_1 = 2.70$ GPa and $\nu_1 = 0.33$ for the current study. For the silicon substrate, in the natural frequency calculations, the following properties were used: $\rho_2 = 2329$ kg/m$^3$, $E_2 = 127$ GPa and $\nu_2 = 0.28$. The adhered individual PVP particles were acoustically excited, and
their vibrating responses were recorded, from which the particle–substrate adhesion properties were extracted. Lateral pushing tests were also performed on adhered PVP particles, and the adhesion properties of the particle/substrate system were extracted from the slope of the pre-rolling part of the pushing force–particle displacement curve.

3. Adhesion Theory

The work of adhesion determination is primarily based on the measurement of the adhesion force between a particle and a substrate. Several contact mechanics models have been developed since the Hertz model to predict the adhesion properties of particles. Some of the adhesion models that are commonly used...
to describe the nature of the adhesion force include the Hertz model, Johnson–Kendall–Roberts (JKR) model [20], Derjaguin–Muller–Toporov (DMT) model [21], Maugis–Dugdale (M–D) theory [22], and Bradley model [23]. The JKR model takes the surface energy and the particle deformation into consideration [20]. The DMT theory predicts that the contact area of the particle tends to zero at the moment of separation [21]. The JKR model is considered to be a good approximation for soft particles, while the DMT model for hard particles. Among the many theories developed, the JKR theory and DMT theory have gained wider acceptance. However, in [24], a unifying framework for these theories (Hertz, JKR, DMT, M–D and Bradley) has been proposed and transition between them has been established for ranges of external loads and the elasticity parameter.

According to the JKR theory, which is essentially a one-dimensional (out-of-plane) model, a particle in contact with a flat substrate induces short range forces (adhesion and elastic forces) between the particle and the substrate, which lead to deformation of the particle and the substrate at the point of contact [20]. When an external lateral force (or rolling moment) is applied on the particle, a moment at the contact point is induced. Above a critical value, this moment results in free-rolling of the particle on the substrate. Rolling motion involves the change of contact area at the leading edge and at the trailing edge of the contact with the surface, resulting in asymmetry of the pressure field, i.e., the leading edge of the contact area establishes new contact and peeling of the trailing edge takes place [25]. This asymmetric pressure distribution results in shifting of contact area, and, consequently, the particle could undergo free rotational oscillations with respect to the contact area [26]. Therefore, a two-dimensional model is necessary for accurate prediction of the moments and deformations. Based on a two-dimensional theory [27], an expression for the rolling resistance moment exhibited by the particle when subjected to a rolling moment is given in [27, 28]. In the JKR adhesion model [20], the contact adhesion force $F_A$ between a spherical particle and flat substrate at static equilibrium is proportional to the particle radius ($r$), $F_A = \frac{3}{2} \pi W_A r$, where $W_A$ is the work of adhesion (Dupré’s energy) between the particle and the substrate. Since the particle mass is proportional to $r^3$, adhesion forces dominate inertial effects in small length scales (i.e., in micro/nano-scales) and short time-scales (i.e., relatively at low frequencies). One consequence of this scaling effect is the possibility of generating low-amplitude high frequency particle vibrations without particle detachment. High-frequency motion of a particle can be excited on its base by a piezoelectric transducer [28]. The resulting displacement of the particle can be resolved into two components: (i) axial displacement as depicted in Figure 2(a), and (ii) angular displacement with respect to the center of the adhesion contact area as in Fig. 2(b). In the current work, the latter component was termed as rocking motion. Since the adhesion properties can be related to the natural frequencies of the vibrational motion of a particle on a surface, the vibrational motion of a particle can be used to deter-
Figure 2. Schematics of the (a) axial and (b) rocking motions of an adhered particle subjected to base excitation and (c) the torsional spring model for the rolling motion of an adhered particle due to a lateral pushing force $F$. 

To determine the particle–surface adhesion properties, the radial natural frequency $\omega_{\text{rigid}}$ of this oscillator for the rocking motion of a spherical particle is described by [2, 3]

$\omega_{\text{rigid}} = 2\pi f_{\text{rigid}} = \frac{1}{r^{3/2}} \sqrt{\frac{45 W_A}{4 \rho}}$,  \hspace{1cm} (1)

where $\rho$ is the mass density of the particle material, $W_A$ the work of adhesion, and $r$ the particle radius. Note that depending on the nature of the elastic bond...
between the particle and the substrate, the particle can undergo rolling with respect

to different centers of rotation. If the particle–substrate system could be assumed

rigid, the center of the rotation of the particle (in rocking motion) is simply the

center of particle itself as the rocking particle rolls on the surface even prior to its

free-rolling motion. On the other hand, in case of the formation of an elongated

neck in the contact area, the center about which the particle rocks is located in the center

of the contact area due to the high elasticity of the particle material compared to the

substrate material. Consequently, the equation of motion changes and the resulting

expression for the radial rocking resonance frequency \( \omega_{\text{neck}} \) becomes

\[
\omega_{\text{neck}} = 2\pi f_{\text{neck}} = \frac{1}{r^{3/2}} \sqrt{\frac{45 W_A}{14 \rho}}.
\] (2)

Equations (1) and (2) relate the work of adhesion between the particle and the sub-

strate and the natural frequencies of the particle rocking motion for two types of

bond structures. When the nature of the bond is not certain, the stiffness of the elas-
tic bond between the PVP particle and the silicon substrate can also be modeled as

a simple torsional spring, as depicted in Fig. 2(c).

As shown in Fig. 2(c), by applying a lateral force \( F \) on the particle, the resisting

moment \( M \) due to rotation \( \theta \) is \( M = Fr = \bar{k}\theta \), where \( \bar{k} \) is the equivalent torsional

stiffness constant of the spring, \( F \) the applied force, and \( r \) the radius of the particle. Assuming that the horizontal displacement of the center of the particle \( \Delta x \) can be

represented as \( \Delta x = \theta r \), it can be shown that

\[
F = \frac{\bar{k}}{r^2} \Delta x.
\] (3)

Introducing \( k^* = \bar{k}/r^2 \) as the slope of the force–displacement curve in contact push-
ing experiments and considering simple rocking motion without damping effect, the

equation for the particle rocking motion is represented as \( Ic\ddot{\theta} + \bar{k}\theta = 0 \), where \( Ic \) is

the moment of inertia of the particle with respect to the contact point. The natural

frequency of the rocking motion is then obtained as

\[
\overline{f}_0 = \frac{1}{2\pi} \sqrt{\frac{5\bar{k}}{16\rho \pi r^5}},
\] (4)

where \( \rho \), \( r \) and \( \overline{f}_0 \) are the mass density, the radius, and the natural frequency of

the micro-spherical PVP particle, respectively. By obtaining natural frequencies of

the rocking motion experimentally, according to equation (4), the corresponding

torsional stiffness value (\( \bar{k} \)) can be found by

\[
\bar{k} = \frac{64}{5} \rho \pi^3 \overline{f}_0^2 r^5.
\] (5)

With equations (4) and (5), comparing and verifying the torsional spring as the bond

model is possible. When the torsional stiffness data are available using contact lat-
eral pushing experiments, the associated range of expected natural frequencies can
be found using equation (4). After conducting base excitation experiments, the natural frequencies of the rocking motion can be found by comparing the differences between the frequency responses of the particle and the substrate (the amplitude peaks of the particle responses that shift with respect to those of the substrate are considered as natural frequencies of the rocking motion). Having the experimentally obtained natural frequencies and using equation (5), torsional stiffness $\bar{k}$ can be calculated, which then can be compared to the previously extracted value of $\bar{k}$ using the lateral pushing technique.

Substantial difference between the out-of-plane stiffness and the rocking stiffness leads to a large difference between the natural frequencies of the out-of-plane motion and the rocking motion of a spherical particle on a substrate. The natural frequencies of rocking motion are considerably easier to detect and to utilize to determine the work of adhesion since, due to its low rocking stiffness compared to the out-of-plane motion; the amplitude of the rocking motion of the particle is much larger than that of the out-of-plane motion. It is also important to note that there exist infinite numbers of planes in which the rocking motion can occur. In this case, the observation of a number of resonance frequencies should be expected for the same particle since adhesion property depends on the direction of motion.

4. Experimental Setup and Procedures

Both noncontact (acoustic base excitation) and a contact (lateral pushing) measurement methods are employed to calculate the rocking motion natural frequencies and consequently the work of adhesion of the PVP particles on flat substrates. The schematics of the experimental setup for base excitation and contact lateral pushing experiments are depicted in Fig. 3. The base excitation technique is based on the detection of the resonance frequencies of the rocking motion of micro-spherical particles. The out-of-plane transient displacement responses of the rocking particles are captured by a laser interferometer, and the natural frequencies of the particle rocking motion are related to the strength of the adhesion bond. In the contact lateral pushing experiments, a lateral force is exerted on a PVP particle in a quasi-static manner, and the resulting displacement of the particle center is recorded as a function of the lateral force. The resulting slope of the pushing force–particle displacement curve is related to the work of adhesion between the particle and the substrate.

4.1. Acoustic Base Excitation Experiment for Work of Adhesion Determination

In the noncontact work of adhesion determination approach, the relation between the rocking natural frequency and the adhesion properties was utilized (equation (1)). To determine the rocking frequency of a particle on a flat substrate, a set of experiments were designed and conducted. PVP particles were dry-deposited on a flat silicon substrate (Polishing Corporation of America, Santa Clara, CA) and sufficient time was allowed for the PVP particles to relax and adhere to the substrate.
The substrate was then placed on a contact transducer with a central frequency of 3.5 MHz (Model V682, Panametrics, Waltham, Massachusetts). Coupling gel was applied between the silicon substrate and the transducer to maximize the acoustic transmission. The transducer was mounted on the $x$–$y$-translation stage of an optical microscope (as depicted in Fig. 2(c)). A charge coupled device (CCD) camera was attached to the optical microscope to monitor the experiments.
A laser Doppler vibrometer (LDV, Polytec, OFV511, Waldbronn, Germany) and a vibrometer controller (OFV3001, Polytec) were integrated with the optical microscope. The laser spot was directed to the top of the particle on the substrate (Fig. 4(a)). Note that only spherical PVP particles were chosen in the reported experiments. The transducer was excited by a square pulse from pulser/receiver (5077PR, Panametrics). The axial (out-of-plane) response of the particle ($\delta$) to the vibrational field was measured using the vibrometer. This procedure was repeated to measure the response of the surface of the silicon substrate to characterize the base motion. The transducer was excited by an electrical pulse with an amplitude of 400 V. It was observed that some of the particles on the substrate tended to agglomerate and form clusters, while others tended to oscillate as single particles (Fig. 4(b)). These single oscillating particles on the substrate were located and examined for rocking frequency measurements. The laser spot of the fiber interferometer unit was focused on a particle using a 100× magnification objective lens. The transient motion of the particle was acquired and saved by an oscilloscope for further signal processing. The translation stage was adjusted to focus the laser spot
Figure 4. Optical microscope images of (a) a PVP particle dry-deposited on the silicon substrate with the laser spot of the interferometer on top of the particle; (b) PVP particle agglomerates on the silicon substrate; and (c) the laser spot on the substrate in the neighborhood of the particle for measuring the base motion. (d) An SEM image of a PVP particle with a diameter of 33 µm on a silicon substrate at 1330× magnification.

on the substrate in the neighborhood of the particle and the substrate response was recorded (Fig. 4(c)). This procedure was repeated for a number of PVP particles with a range of diameters on the substrate, and the corresponding waveforms were digitized and saved for further signal processing. The natural frequencies of the adhesion bond were identified by applying a Fast Fourier Transform (FFT) routine to
the acquired transient responses of the particle and the substrate. Equation (1) was utilized to extract the work of adhesion of particle–substrate bond from the natural frequencies of the rocking motion. An SEM image of a PVP particle dry-deposited on a silicon substrate at $1330 \times$ magnification is shown in Fig. 4(d). All the base excitation experiments reported in this study were conducted in ambient condition.
4.2. Lateral Pushing Experiment for Work of Adhesion Determination

The work of adhesion values extracted using the noncontact base excitation technique were compared with those obtained using the contact rolling resistance moment-based lateral pushing technique [28]. The rolling resistance moment-based lateral pushing experimental setup is depicted in Fig. 5(a). When a lateral pushing force is applied to an adhered particle, the stress distribution in the particle–substrate contact region becomes non-uniform. Such non-uniform stress distribution will create a restoring moment (also referred to as resistance moment) to resist the rolling motion, and this moment is proportional to the angle of rotation of the particle. When the lateral force exceeds a certain threshold, this resistance is overcome and the particle begins to roll on the substrate. For the lateral pushing experiments, the same type of spherical PVP particles were employed. Particles were selected such that their diameters were comparable to the ones used in the non-contact base excitation experiments. PVP particles were dry-deposited on a silicon substrate (Polishing Corporation of America). In the experiments, a lateral pushing force \( F \) was applied to an adhered PVP particle by a tipless AFM cantilever beam with a length of 350 \( \mu \text{m} \) (CSC 38, MikroMasch, Inc., Tallinn, Estonia) such that a rolling moment with respect to the bonding area was generated with a moment arm of the PVP particle radius (Fig. 5(b)). All the contact lateral pushing experiments were conducted with the aid of a custom-made nanomanipulator (Fig. 5(a)).

![Figure 5](image)

**Figure 5.** (a) A close-up photograph of the lateral pushing test experimental setup; (b) an optical microscope image of the pushing of a 31.9 \( \mu \text{m} \) PVP particle with a tipless AFM cantilever probe; and (c) the free-body diagram of a particle with an adhesion force \( F_A \), a moment \( M_Y \) resisting its rolling under a lateral force \( F \) causing a lateral translation of \( \xi \) (contact area is not to scale).
nanomanipulator has two opposing positioning stages consisting of two integrated $X$–$Y$–$Z$ linear motion stages (122-1135/1155, OptoSigma, Inc., Santa Ana, California) on the opposing planes. The stages are driven by piezoelectric actuators (MRA 8351, New Focus, Inc., Santa Clara, California) that provide linear motion with a
motion resolution of approximately 30 nm. A piezoelectric bender (CMBP 05, Noliac A/S, Denmark) that provides fine positioning at sub-nanometer resolution is mounted on one of the stages (Fig. 5(a)). For the pushing trials, the base chip of the cantilever was attached at the free end of the piezoelectric bender, and the silicon substrate with the PVP particles deposited was mounted on the opposing stage. The nanomanipulator allows precise positioning and motion of the tip of the cantilever beam with respect to the PVP particles on the silicon substrate.

In the contact pushing experiments, the cantilever was first brought into close proximity of a selected PVP particle on the substrate through a series of translational motions of the stages of the nanomanipulator. Then a dc (direct current) voltage incremented in discrete steps was applied to the piezoelectric bender to actuate the AFM cantilever until the cantilever came in contact with the PVP particle at point C (Fig. 5(b) and 5(c)). Since motion of the cantilever became constrained by the adhesion bond and the associated rolling resistance at the particle–substrate interface, the cantilever began deflecting as a lateral force was externally exerted on the PVP particle moving from C to C’ (Fig. 5(c)). The pushing force was increased in discrete steps (10–15 nN per step) in a time interval of approximately 30 s. By acquiring a series of digital images, the entire pushing process was recorded for each PVP particle tested.

The AFM cantilever served as the force sensing element. The applied force (F) was calculated from the relative cantilever deflection using the linear bending stiffness of the cantilever beam. The relative deflection of the cantilever beam at each pushing step was obtained with a previously developed piezoelectric bender response calibration procedure [29]; and the bending stiffness of the cantilever beam was calibrated in the ambient conditions before the test with a resonance method [30]. The displacement of the particle in the x-direction (Δx) was obtained from the processing of recorded images by tracking the pixel positions of the particle in the recorded digital images. In current contact lateral pushing experimental configuration, small contact areas and no sliding between the particle and the substrate in the initial phases of the pushing are assumed. The rolling moment M induced by the pushing force (F) with respect to the contact area on the substrate can be approximated as $M \approx F \times (D/2)$, and the angle of rotation (θ) of the particle can be approximated from the measured displacement (Δx) as $\theta \approx \tan \theta \approx \Delta x/(D/2)$, assuming the particle rotation is small and that the displacement at the particle center is the same as the displacement at particle–cantilever contact point (C). A force–displacement (F – Δx) curve can then be constructed for each PVP particle tested with the pushing force and particle displacement information at each pushing step. The work of adhesion between the particle and the substrate can then be determined from the response of the particle to the lateral pushing force. In the current study, the slope of the force–displacement curve ($k^*$) can be approximated in a displacement range corresponding to the pre-rolling phase of motion as [28]

$$k^* = \frac{F}{\Delta x} = \frac{M/(D/2)}{\theta/(D/2)} = \frac{4M}{\theta D^2},$$

(6)
where $M$ is the moment generated by the pushing force with respect to the particle–substrate contact area, $\theta$ the angle of rotation of the particle with respect to the center of particle–substrate bond, and $D$ the diameter of the spherical particle. According to Dominik and Tielens [27], the rolling resistance moment as a function of the angle of rotation $\theta$ can be approximated as

$$M \approx 6\pi W_A (D/2)^2 \theta,$$

(7)

where $W_A$ is the work of adhesion between the particle and substrate. Therefore, from equations (6) and (7), the work of adhesion is directly proportional to slope of the force–displacement curve, i.e., $W_A = k^*/6\pi$. It is noteworthy that, with this approach, no knowledge of the particle diameter is required for determining the work of adhesion between the particle and the substrate. All the contact lateral pushing experiments reported in this study were conducted in ambient conditions.

5. Results and Discussion

In the contact lateral pushing experiments, a set of eight spherical PVP particles were tested, and they were grouped into two sets according to their diameter ranges as follows: Group A (33.4 µm, 36.9 µm, 44.3 µm, 50.8 µm and 56.1 µm in diameter) and group B (25.3 µm, 26.1 µm and 31.9 µm in diameter). As an incremental force was exerted on the particle, the AFM cantilever deflection and particle displacement at each pushing step were obtained through the image analysis procedure described in Section 4, and the force ($F$)–displacement ($\Delta x$) relationships were extracted (Fig. 6). It is clear that the displacement of the particle increases with increasing pushing force as the particle rotates. Above a certain level of force for each particle (with an exception of group B), it was observed that the external force dropped rapidly as the particle displacement in the direction $x$ increased substantially. This observation suggests that the particle–substrate adhesion bond was broken and/or significantly weakened, and the particle slid without rolling. The maximum forces prior to this sudden drop (possibly due to loss of contact), as depicted for the particles in Fig. 6(b), range from 450 to 3250 nN. The experimental force–displacement data depicted in Fig. 6(a) indicate the slope of the force–displacement curve ($k^*$) varies for each trial, especially between the two groups. The initial parts of the eight curves are depicted in Fig. 6(b). In the pushing trials for group A, the initial particle displacement is due to the pre-rolling motion of the particle. The sudden slope change indicates that the adhesion bond yields (or breaks), the leading edge of the bond closes as the trailing end opens and loses its ability to resist rolling. For group B, the rolling resistance might be too small to be detected with the current setup, and thus these particles appear to start rolling instantly upon the exertion of force with no rolling resistance. The contact rolling experimental data for the PVP particles examined are reported in Table 1. The work of adhesion between the PVP particle and the silicon substrate was calculated from the pre-rolling slope of each force–displacement curve (Fig. 6).
Figure 6. (a) Force–displacement curves for the eight spherical PVP particles (with their diameters shown in μm) under lateral pushing force $F$ and (b) a close-up of the initial parts of the curves.

By having the relation between torsional stiffness of the bond $\tilde{k}$ with the slope of force–displacement curve $k^*$, the corresponding $\tilde{k}$ value can be calculated using equation (4). Once the $\tilde{k}$ values are calculated for PVP particles, the corresponding range for expected natural frequencies of the rocking motion on flat substrates $f_0$
Table 1.
Summary of the values of the measured pre-rolling stiffness \(k^*\), free-rolling stiffness \(k^*_o\), critical distance \(\xi\), critical angle of rotation \(\theta\) in the lateral pushing experiments and the corresponding work of adhesion values calculated based on the pre-rolling stiffness

<table>
<thead>
<tr>
<th>Particle diameter (µm)</th>
<th>Pre-rolling stiffness (k^*) (N/m)</th>
<th>Free-rolling stiffness (k^*_o) (N/m)</th>
<th>Critical distance ((\text{onset of rolling})) (\xi) (nm)</th>
<th>Critical angle of rotation (\theta) ((\times 10^{-3}) rad)</th>
<th>Work of adhesion (W_A) (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>33.4</td>
<td>2.55</td>
<td>1.12</td>
<td>214</td>
<td>13 (0.74°)</td>
<td>135.4</td>
</tr>
<tr>
<td>36.9</td>
<td>2.63</td>
<td>1.22</td>
<td>257</td>
<td>14 (0.80°)</td>
<td>139.6</td>
</tr>
<tr>
<td>44.3</td>
<td>2.43</td>
<td>1.01</td>
<td>257</td>
<td>12 (0.68°)</td>
<td>129.0</td>
</tr>
<tr>
<td>50.8</td>
<td>2.92</td>
<td>1.95</td>
<td>228</td>
<td>9 (0.51°)</td>
<td>155.0</td>
</tr>
<tr>
<td>56.1</td>
<td>2.98</td>
<td>1.63</td>
<td>514</td>
<td>18 (1.03°)</td>
<td>158.2</td>
</tr>
</tbody>
</table>

The rocking resonance frequencies were extracted from the frequency responses of PVP particles on flat substrates using base excitation experiments. The experimental procedure developed for the base excitation study was applied to a set of 30 PVP particles dry-deposited on a silicon substrate. However, the out-of-plane transient and frequency responses of seven PVP particles of this set with different diameters (between 33 and 56 µm) are reported here. The time and frequency domain responses of the PVP-silicon systems are depicted in Fig. 7. Determined rocking frequencies were used to extract the work of adhesion values based on equation (1) and the range of torsional stiffness of the adhesion bond between PVP particles and flat substrates \(\bar{k}\) using equation (5). These calculated \(\bar{k}\) values along with the \(k^*\) values obtained from contact lateral pushing experiments and the calculated work of adhesion values for different particles are shown in Table 3.
Table 2.
Summary of the values of the measured pre-rolling bond stiffness $k^{*}$ in the lateral pushing experiments along with the corresponding ranges of torsional spring stiffness $k$ (based on $k^{*}$) and the natural frequencies of the rocking motion ($f_0$, $f_{\text{neck}}$ and $f_{\text{rigid}}$) calculated using the range of $k$ for the reported PVP particles

<table>
<thead>
<tr>
<th>Particle diameter range (µm)</th>
<th>Pre-rolling stiffness $k^{*}$ (N/m)</th>
<th>$k$ ($\text{N m rad}^{-1}$) $\times 10^{-10}$</th>
<th>$f_0$ (kHz)</th>
<th>$f_{\text{neck}}$ (kHz)</th>
<th>$f_{\text{rigid}}$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>33.4 ± 0.5</td>
<td>2.55</td>
<td>6.69</td>
<td>32.30</td>
<td>42.29</td>
<td>79.13</td>
</tr>
<tr>
<td>36.9 ± 0.5</td>
<td>2.63</td>
<td>8.47</td>
<td>28.36</td>
<td>37.14</td>
<td>69.49</td>
</tr>
<tr>
<td>44.3 ± 0.5</td>
<td>2.43</td>
<td>11.39</td>
<td>20.86</td>
<td>27.32</td>
<td>51.12</td>
</tr>
<tr>
<td>50.8 ± 0.5</td>
<td>2.92</td>
<td>18.10</td>
<td>18.71</td>
<td>24.49</td>
<td>45.83</td>
</tr>
<tr>
<td>56.1 ± 0.5</td>
<td>2.98</td>
<td>22.62</td>
<td>16.33</td>
<td>21.88</td>
<td>39.99</td>
</tr>
</tbody>
</table>

Table 3.
Summary of the values of the torsional spring stiffness $k$ and work of adhesion values calculated from the acoustically determined natural frequencies and the pre-rolling bond stiffness $k^{*}$ determined from the lateral pushing experimental data for the reported PVP particles

<table>
<thead>
<tr>
<th>Experiment type</th>
<th>Particle diameter range (µm)</th>
<th>Pre-rolling stiffness $k^{*}$ (N/m)</th>
<th>Torsional stiffness $k$ ($\text{N m rad}^{-1}$) $\times 10^{-10}$</th>
<th>Work of adhesion $W_A$ (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base excitation</td>
<td>35.6 ± 0.5</td>
<td>n/a</td>
<td>8.89 ± 1.09</td>
<td>130.3</td>
</tr>
<tr>
<td>Contact rolling</td>
<td>33.4 ± 0.5</td>
<td>2.55</td>
<td>7.11 ± 0.43</td>
<td>135.4</td>
</tr>
<tr>
<td>Base excitation</td>
<td>36.3 ± 0.5</td>
<td>n/a</td>
<td>6.14 ± 2.30</td>
<td>133.7</td>
</tr>
<tr>
<td>Contact rolling</td>
<td>36.9 ± 0.5</td>
<td>2.63</td>
<td>8.95 ± 0.49</td>
<td>139.6</td>
</tr>
<tr>
<td>Base excitation</td>
<td>45.2 ± 0.5</td>
<td>n/a</td>
<td>12.03 ± 5.66</td>
<td>129.8</td>
</tr>
<tr>
<td>Contact rolling</td>
<td>44.3 ± 0.5</td>
<td>2.43</td>
<td>11.92 ± 0.54</td>
<td>129.0</td>
</tr>
<tr>
<td>Base excitation</td>
<td>51.5 ± 0.5</td>
<td>n/a</td>
<td>23.10 ± 10.87</td>
<td>152.6</td>
</tr>
<tr>
<td>Contact rolling</td>
<td>50.8 ± 0.5</td>
<td>2.92</td>
<td>18.97 ± 0.61</td>
<td>155.0</td>
</tr>
<tr>
<td>Base excitation</td>
<td>55.8 ± 0.5</td>
<td>n/a</td>
<td>34.50 ± 16.23</td>
<td>163.5</td>
</tr>
<tr>
<td>Contact rolling</td>
<td>56.1 ± 0.5</td>
<td>2.98</td>
<td>23.47 ± 0.82</td>
<td>158.2</td>
</tr>
</tbody>
</table>

From the time responses of particle–substrate pairs under base excitation (Fig. 7), it is evident that the substrate response due to the acoustic base excitation diminishes faster than that of the particle. This behavior was observed for most of the PVP particles in the experimental set. However, since the spherical particle is adhered to a flat surface, multiple rocking frequencies were detected. Such phenomenon is expected because there exist infinite numbers of planes in which the rocking motion can occur for a spherical particle adhered to a flat substrate. The observation of multiple rocking frequencies indicates that adhesion property depends on the direction of motion. In Fig. 7, the solid circles show the selected rocking frequencies for each PVP particle for work of adhesion calculation, while multiple rocking frequencies are marked with dashed line ellipses. The dashed line rectangular boxes show the
Figure 7. Temporal and spectral responses of the substrates (solid lines) and seven PVP particles (dashed lines) with diameters of (a) 25.9 µm, (b) 26.4 µm, (c) 35.6 µm, (d) 36.3 µm, (e) 45.2 µm, (f) 51.5 µm and (g) 55.8 µm. The locations of the selected rocking frequencies for work of adhesion calculations are marked with solid circles, the locations of multiple rocking frequencies are marked with dashed line ellipses, and the dashed line rectangular boxes show the range of natural frequencies used to calculate the torsional stiffness of the adhesion bond.

range of natural frequencies that is used to calculate the torsional stiffness of the adhesion bond.

6. Conclusions and Remarks
In the current study, for the first time, a noncontact base excitation technique was demonstrated for characterizing the adhesion behaviors of a commonly used round-shaped tablet binder, PVP. The main advantage of the noncontact method in work of adhesion determination used in this study is that it eliminates the reported shortcom-
ings of contact-based methods (e.g., AFM). In this technique, the natural frequency of the rocking motion of the particle on a flat substrate subjected to base motion was identified as the key frequency in determining the particle adhesion properties. It is observed that the measured particle displacements are predominantly due to rocking motion and the frequencies corresponding to axial motion are absent. The work of adhesion values of PVP particles to silicon substrates were calculated with a range of particle diameters. For comparison purposes, the work of adhesion values of the PVP microparticle-silicon substrate system were determined using a rolling resistance moment-based lateral pushing technique. In this technique, a lateral pushing force was applied to an adhered PVP particle with a custom-made nanomanipulation system under an inverted optical microscope. The response of the particle to the lateral pushing force was obtained, and the work of adhesion
between the particle and the silicon substrate was deduced from the slope of the pre-rolling part of the force–displacement curve. The work of adhesion values extracted from the base excitation technique were compared to those determined from the lateral pushing experiments. A good agreement was observed between the results obtained with these two techniques. Due to the existence of the infinite numbers of planes in which the rocking motion can occur, a number of resonance frequencies for the same particle were observed as expected. In order to characterize the particle/substrate adhesion bond, different modes (rigid contact, neck-shaped contact, and an equivalent torsional spring) in the contact area were considered, and the required formulations governing each case were derived. For each case, the expected natural frequencies of the particle rocking motion were extracted from the slopes of force–displacement curves which were obtained in the contact lateral pushing
experiments. The existence of all possible modes of the particle/substrate bond was verified because all expected natural frequencies corresponding to each case in the particle/substrate response were observed in base excitation experiments.

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Figures 7. (Continued.)
Figure 7. (Continued.)
Figure 7. (Continued.)

References