From Adhesion to Wetting: Contact Mechanics at the Surfaces of Super-Soft Brush-Like Elastomers

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ABSTRACT: Fundamental understanding of rigid particle indentation into soft elastic substrates has been elusive for decades. In conventional heterogeneous and multicomponent systems, the ill-defined interplay between elastic and capillary forces has confounded explanation of the crossover region between the classical wetting and adhesion regimes. Herein, we study the indentation behavior of micrometer-sized silica particles on supersoft, solvent-free PDMS elastomers with brush-like network strands. By varying the side chain grafting density and the cross-linking density of the networks, we control their elastic modulus from ~1 to 100 kPa without adding solvent. This isostructurally regulated balance between elastic and capillary forces allows for accurate mapping of the entire range of particle–substrate interactions by measuring indentation depth as a function of substrate stiffness and particle radius. A generalized theoretical model, accounting for the collaborative contribution of both forces to the system free energy, demonstrates excellent quantitative agreement with our experimental results as well as with results of computer simulation for particles in contact with soft surfaces.

Spontaneous indentation of rigid particles into a soft substrate upon adsorption is vital for understanding a broad range of applications including emulsion stabilization,1,2 particulate adhesives,3–5 and lung clearance.6–8 Depending on the particle dimensions, substrate modulus, and particle–substrate interfacial interactions, particles may either rest on the substrate surface or completely submerge and become engulfed by the substrate. The classical solution to this problem is known for two limiting cases: (i) a particle in contact with a liquid (the wetting regime) and (ii) a particle in contact with an elastic solid (the adhesion regime). In the first case, the immersion depth below the liquid surface is controlled by capillary forces; while in the case of the elastic solids, the indentation depth is determined by the balance between counteracting adhesive and elastic forces as described by the Johnson, Kendall, and Roberts (JKR) theory.9 However, explaining the dependence of the indentation depth on the substrate surface tension, γ, work of adhesion between substrate and particle, W, and substrate shear modulus, G, in the entire interval of substrate deformations produced by a particle with size R, as shown in this paper, requires simultaneous consideration of both capillary and elastic forces. This analysis results in the expression for a critical particle size, R* ≈ γ1/2W−1/2G−1/2, defining crossover between wetting (Rp < R*) and adhesion (Rp > R*) regimes.

In order to experimentally verify this complex behavior and measure particle indentation depth in the crossover between the wetting and adhesion regimes, elastic substrates with shear moduli in the kPa range are required. So far, materials of this type have been available only in the form of gels, that is, mixtures of liquids and polymer networks.10 However, the contact mechanics of gels may be affected by the unremitting variation of their liquid fractions upon indentation and phase separation at the contact line,11 which may shift both capillary and elastic forces. Therefore, to achieve kPa moduli, we use solvent-free elastomer substrates made by cross-linking brush-like strands (Figure 1).12–15 The brush-like architectures promote disentanglement of the network strands and, hence, allow for significant (several orders of magnitude) reduction of the modulus.12 Specifically, without altering the chemical composition or adding solvent, the modulus can be controlled in a broad range from 102 to 105 Pa by varying the three architectural parameters (n, n, n).14 Herein, we vary n to achieve substrates with shear modulus in the kPa range. Critically, the solvent-free and isostructural nature of these substrates eliminates any compositional variation at the contact interface, and we are thus able to accurately map the entire range of contact phenomena, from liquid-like wetting to solid-like adhesion, for single-component elastic solids. Further, the distinct softness of the substrates allows for the use of micrometer-sized particles as indentation probes. The micron dimensions not only facilitate measurement precision, but are

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The equilibrium deformation of the substrate is obtained by minimizing eq 1 with respect to $\Delta h$, which results in the following expression

$$\partial \Delta F/\partial \Delta h = -2\pi WR_p \Delta h + 2\pi \Delta h^2 + \frac{16}{\sqrt{3}} GR_p^{1/2} \Delta h^{5/2} = 0$$

Balance of the first and second terms in eq 2 results in $\Delta h/R_p = W/\gamma_s$, the equilibrium indentation depth determined by work of adhesion and surface tension. In this so-called wetting regime, the indentation does not depend on the substrate stiffness. Similarly, balancing the first and last terms in eq 2 leads to $\Delta h/R_p \propto (W/GR_p)^{2/3}$, the classical JKR expression for indentation depth, which is controlled by the substrate modulus $G$. We call this the adhesion regime. By equating the above expressions for indentation depth, we obtain the dimensionless parameter $\gamma_s (GR_p)^{-2/3} W^{1/3}$, which describes the relative strength of elastic and capillary forces. At $\gamma_s (GR_p)^{-2/3} W^{1/3} \approx 1$, the crossover corresponds to an indentation depth of $\Delta h \approx W^{1/2} r_s^{1/2}/G$. Note that complete submersion of the particle (i.e., the point at which $\Delta h \approx 2R_p$) occurs at $W = \gamma_s \Delta h/R_p \approx 2\gamma_s$. The outlined regimes and the crossovers between them are depicted in Figure 2. It is worth pointing out that in the case of pure dispersion forces, for which the work of adhesion $W = 2R_p \sqrt{\gamma_s \gamma_s}$, a condition for the particle to remain above a substrate in the wetting regime reduces to $\gamma_p < \gamma_s$.

The above model of particle-substrate interactions was tested by direct measurements of the indentation depth $\Delta h$ of monodisperse, rigid, silica microspheres ($R_p = 0.2 \text{–} 1.5 \mu m$) deposited on various bottlebrush, comb-like, and linear chain PDMS networks. As highlighted above, these brush-like architectures allow for precise variation of stiffness well below 100 kPa (Table 1 summarizes corresponding shear moduli ranging from $\sim 3$ to 80 kPa along with other molecular and mechanical characteristics). Yet, to ensure continuous crossover with the adhesion regime, we also synthesized two linear-strand PDMS elastomers having moduli of 32 and 58 kPa. In every case, we characterized the elongation of the elastomers by conducting loading–unloading cycles for a broad range of strains (Figure 2.1b), demonstrating reversible hyperelasticity for the brush-like elastomers. Modulus and elongation-at-break were deduced from stress–strain curves measured during uniaxial extension (Figure S2.1a).

Figure 3 displays snapshots of different particle-substrate configurations as a function of $R_p$ and $G$. For each configuration, surface profiles from SEM images were analyzed to obtain $\Delta h = 2R_p - h$ from the height of particle $h$ above the substrate surface (Figure S2.2). Generally, indentation ($\Delta h$) decreases monotonically with increasing substrate stiffness and particle size (Table S2.1). For example, the hardest substrate ($G = 583.0$ kPa) is the most “particle-phobic”, which is attributed to the greater energetic penalty of elastic deformation predicted for more rigid substrates and larger particles (eq 2). On the other hand, smaller particles on softer substrates exhibit higher “affinity” for the substrates, characterized by larger indentation and formation of a meniscus at the contact line (Figure S2.3). For the softest substrate ($G = 3.3$ kPa), micrometer-sized particles submerge almost completely, mimicking the classical behavior of particles adsorbed at air–liquid interfaces.
The above scaling relationships between indentation depth, particle size, and substrate shear modulus are analyzed in Figure 4 by plotting $G\Delta h$ as a function of $GR_p^*$ to collapse all of the data sets measured in the broad ranges of substrate stiffness ($G \cong 3$–600 kPa) and particle size ($R_p = 0.2$–1.5 μm). The plot displays two distinct scaling regimes for the equilibrium indentation depth. In the wetting regime, the indentation depth is directly proportional to the particle size as $\Delta h \sim R_p$ while in the adhesion regime it scales with both particle size and modulus as $\Delta h \sim R_p^{1/3}G^{-2/3}$. The 1 and $1/3$ exponents of the power laws are consistent with the two limiting solutions of eq 2.

We can therefore calculate the work of adhesion $W$ and the substrate surface tension $\gamma_s$ for the PDMS/silica particle systems by fitting our experimental data to eq 2 with two fitting parameters: $W$ and $\gamma_s$. From this analysis, we obtain a PDMS/silica work of adhesion of $W = 47.4 \pm 3.0$ mN/m and a PDMS surface tension of $\gamma_s = 23.6 \pm 2.1$ mN/m (see SI for details). The obtained surface tension value is consistent with literature data.21,22 Yet, our results differ with respect to the corresponding values $W = 81.8 \pm 1.2$ mN/m and $\gamma_s = 45.2 \pm 1.2$ mN/m reported by Style et al., who ascribe the notably higher $\gamma$ value to the effect of surface stress.23 We are not entirely sure about the cause of this discrepancy. However, we note that although the effect cited by Style et al. may be significant in solid materials, its contribution is negligible in liquid-like PDMS elastomers that have both glass transition and melting temperatures considerably below the temperature of the indentation tests.

By refitting Style’s data in terms of the indentation depth (calculated from the contact radius $a$), we obtain surface tension $\gamma_s = 25.8 \pm 1.1$ mN/m and work of adhesion $W = 54.6 \pm 1.0$ mN/m (see SI for fitting analysis details). Further, we observe that our and Style’s data sets generally overlap, with minor discrepancy (15%) for only very soft substrates (the strongest deviation of Style’s data from theoretical prediction is observed in the region where $GR_p < 10$, that is, for the softest substrate, $G = 1 \text{ kPa}$, with the largest fraction of linear PDMS). One explanation of this discrepancy is that larger indentations, in softer substrates or by larger particles, cause more significant solvent variation (a factor eliminated in the current work by the solvent-free nature of the substrates). These details aside, it is important to point out that $W > 2\gamma_s$ for both sets of data. Thus, in the absence of an elastic response in a network, silica particles will submerge when placed on the PDMS surface. This is supported by our data for particles with $R_p = 0.2 \mu m$ and $R_p = 0.5 \mu m$ on the softest substrates, as shown in Figure 3.

Significantly, knowing both $\gamma_s$ and $W$ allows comparison of our experimental results with those obtained from computer simulations and other studies.16,18,23,24 To facilitate these comparisons, we use the reduced variables21,24 $y_h = \Delta h/\Delta h^*$ and $x_p = R_p/R^*$, where

$$
\Delta h^* = \gamma_s^{1/2}W^{1/2}G^{-1/2}; \quad R^* = \gamma_s^{1/2}W^{1/2}G^{-1/2}
$$

(3)

These reduced variables simplify eq 2 as

$$
0 = -x_p + y_h + \frac{8}{\pi \sqrt{3}} x_p^{1/2} y_h^{3/2}
$$

(4)

Solving eq 4 for $x_p$ in terms of $y_h$ we obtain

$$
x_p = (\delta y_h^{3/2} + \sqrt{\delta y_h^{3/2} + 4y_h^2})^2 / 4
$$

(5)

where $\delta = 8/\pi \sqrt{3} \approx 1.47$ is a numerical constant. Figure 5 presents experimental data together with simulation results using reduced variables. Nearly perfect collapse of the experimental and simulation data confirms validity of the theoretical model and the universality of particle-substrate interactions. Specifically, in accordance with eq 5, the data follow $\Delta h/\Delta h^* \approx R_p/R^*$ in the wetting regime, and $\Delta h/\Delta h^* \approx (R_p/R^*)^{1/3}$ in the adhesion regime. Note that the collapse of experimental and simulation data corroborates our estimation of the work of adhesion $W$ for our PDMS/silica particles’ systems.

In conclusion, we have verified the crossover between the classical wetting and adhesion regimes by measuring the spontaneous indentation of micrometer-sized rigid silica particles into supersoft, solvent-free, brush-like PDMS elastomer substrates. By controlling the architecture of the brush-like network strands as well as using linear chain networks, we were able to cover an unprecedented range of moduli from about 3 to 600 kPa without altering the chemical composition (PDMS) or swelling in a solvent. The experimental data displayed excellent agreement with computer simulation results for the entire interval of system parameters, which corroborates theoretical predictions for particle-induced indentation.16,24
The established crossover between these regimes can be described in terms of critical particle size $R^* = \gamma / \gamma' W^{1/2} G^{-1}$. For smaller particles $R < R^*$, the related equilibrium indentation depth is determined by capillary forces and is independent of the substrate’s elastic properties (wetting regime). However, the equilibrium indentation depth for larger particles ($R > R^*$) is determined by the optimization of the elastic energy of substrate deformation and the work of adhesion in the contact area. This so-called adhesion regime is well-described by the JKR model. Note that $R^*$ depends on all three parameters ($\gamma$, $W$, and $G$) and, for soft substrates ($G \geq 1$ kPa), may achieve micrometer size scale. This is relevant for many biological systems, such as airborne particles inhaled by the lung,6 and the fundamental insights obtained herein could therefore have vital implications for tribology,25 medicine,26 and materials engineering.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.7b00419.

Derivation of the adhesion/wetting model, sample preparation and characterization details, image analysis, data analysis details, and comparison with other experimental data (PDF).

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Notes
The authors declare no competing financial interest.

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