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Adhesion between submicrometer polystyrene spheres

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ABSTRACT

The sphere–substrate contact method was usually used to study adhesion theory because it is rather difficult to make two micrometer or submicrometer spheres contact precisely. Here, we used sphere–sphere contact method by a novel, simple process to investigate deformations of spheres. The polystyrene particles size ranges from 60 nm to 600 nm. We found that the polystyrene particles underwent plastic deformations due to van der Waals interaction. The contact radii were observed by the scanning electron microscope (SEM).

1. Introduction

Deformation behavior of particles plays an important role in many areas such as semiconductor technology and drug delivery [1–3]. In the past 40 years, much work has been done to study the mechanism of the particle deformation resulting from adhesive contact [4–10]. Several models were proposed on this subject. In 1971, Johnson, Kendall and Roberts [4] (hereafter referred to as JKR) revealed that the contact radius varied as the particle radius to the 2/3 power in the absence of the externally applied load. Then, Derjaguin, Muller and Toporov [5] (hereafter referred to as DMT) showed the 2/3 power-law dependence of contact radius upon the particle radius under the zero load. They calculated the contact radii based on the molecular interaction. It was found that the deformation of the particles was caused by the repulsive components of the interaction forces. Both JKR and DMT models assumed that the contact radii were small and only elastic deformation occurred. However, the values of the contact radii predicted by DMT model were approximately 69% of those based on JKR theory. The contact radius can be given as Eq. (1) (JKR model) and Eq. (2) (DMT model), respectively.

$$a^3 = \frac{6\pi w_a R^{*2}}{K} \tag{1}$$

$$a^3 = \frac{2\pi w_a R^{*2}}{K} \tag{2}$$

where a is the contact radius, R^* is equivalent radius of the spheres defined as

$$R^* = \left(\frac{1}{R_1} + \frac{1}{R_2}\right)^{-1} \tag{3}$$

w_a is the work of adhesion, which is defined as

$$w_a = \gamma_p + \gamma_s - \gamma_{ps} \tag{4}$$

where r_p and r_s, are the surface energies of the particle and the substrate, respectively, and r_{ps} is their interfacial energy; and

$$K = \frac{4}{3\left[\frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}\right]} \tag{5}$$

where E_1, E_2, ν_1 and ν_2 are the Young's moduli and Poisson's ratios of two contacting spheres, respectively.

Muller, Yushchenko and Derjaguin [6] (hereafter referred to as MYD) later introduced a general theory, in which JKR and DMT models were valid for the different cases. They indicated that for the case of large particles, higher surface energy, and lower Young's modulus, JKR model is applied; for the case of small particles, lower surface energy, and higher Young's modulus, DMT model is valid. Tabor [7] noted the existence of a neck around the contact area in the JKR contact. He defined a dimensionless parameter μ (Tabor number), which was the ratio of the neck height to the intermolecular spacing. Tabor number was used to quantitatively distinguish the ranges of each model. JKR model is generally applicable to the

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systems of $\mu>3$, while DMT model is valid for the systems of $\mu<0.1$. The dimensionless parameter μ is given as

$$\mu = \left[\frac{R^*(w_a)^2}{E^{*2}z_0^3}\right]^{\frac{1}{3}} \tag{6}$$

where z_0 is the separation distance between the particles and the substrate, the value of 0.4 nm is often used; E^* is equivalent Young's modulus defined as

$$E^* = \left[\frac{1-v_1^2}{E_1}+\frac{1-v_2^2}{E_2}\right]^{-1} \tag{7}$$

In 1984, Maugis and Pollock [8] (hereafter referred to as MP) extended the JKR model to include the plastic deformation. They argued that particles can be elastically, elastoplastically or fully plastically deformed under different conditions. They proposed that the power-law dependence of contact radius upon the particle radius was 0.5 for the case of fully plastic deformations. In this model, if there is no applied load, the contact radius can be given as

$$a = \left(\frac{2w_a}{3Y}\right)^{\frac{1}{2}}R^{*\frac{1}{2}} \tag{8}$$

where Y is yield point of spheres.

In addition to the above analytical elastic, plastic contact models with adhesion, which gave simplifying assumptions, recently, a few more accurate numerical theories of adhesive contact were published [11,12]. Du et al. [11] proposed a numerical model for a single load–unload cycle of an adhesive elastic–plastic spherical contact. A parameter S was suggested to represent the degree of unloading plasticity. They predicted that $S>1$ may lead to ductile separation. The parameter S shown in Eq. (9) is the ratio of the maximum Lennard–Jones stress to the hardness.

$$S = \frac{w_a}{z_0 H} \tag{9}$$

where H is hardness of the material, which is equal to $2.8Y$. Kadin believed that three key parameters can affect the contact and separation modes. These three parameters are Tabor parameter μ, plasticity parameter S, and interference.

As a complement to the modeling work, many experimental jobs related to microcontact with adhesion were conducted. The experimental studies mainly included the measurement of contact radius and adhesion force.

During the research for the measurement of contact radius, two methods were usually utilized: (1) the sphere–sphere contact; (2) the sphere–substrate contact. In the early study, researchers mainly focused on the deformation of the millimeter or centimeter spheres. The sphere–sphere contact method was mainly used [13–16]. When the scope of the investigation on the deformation mechanism extended to the micrometer and submicrometer regimes, the sphere–substrate contact method was usually used because it is rather difficult to make two micrometer or submicrometer spheres contact precisely [17–20]. Unfortunately, the sphere and the substrate usually made from different materials introduced some errors into the calculation, and their different geometrical shapes also brought some errors in the measurement. Thus, it is necessary and meaningful to find a way to make two micrometer or submicrometer spheres contacted.

Atomic force microscope (AFM) [21], Scanning electron microscope (SEM) [22], and Scanning force microscope (SFM) [23] were used to directly measure adhesion force of particles in different media (air [22], water [24], or solution [25]). Hodges et al. [24] measured adhesion forces between polystyrene particles in water using AFM. When the surface roughness of particles was considered, and a calculated optimum value of the surface energy is used to predict the adhesion forces based on JKR model, experimental results were in good agreement with theoretical prediction. Cleaver et al. [26] studied the influence of relative humidity and applied load on adhesion between polystyrene particles using AFM. They found JKR model was valid for describing adhesion under applied load of smaller than 1200 nN over the range of 0–65% RH when surface roughness effect was considered, while MP was valid under applied load of 1200–3500 nN at 65% RH. Thus, the mechanism of adhesion between identical polystyrene particles is still in debate.

In this paper, a novel, simple process was designed to bring two submicrometer polystyrene spheres in contact. The polystyrene particles size ranges from 60 nm to 600 nm. The particles generated the deformation due to attractive forces. The deformation mechanism was discussed. It is very difficult to make two micrometer or submicrometer spheres contact precisely by the old techniques. Our method improves the sphere–sphere contact method and further elucidates the mechanism of adhesion between polystyrene particles.

2. Experimental methods

The experimental process is listed below: 1 g of polystyrene sphere was diluted into the solution. The concentration of polystyrene spheres in alcohol was approximately 0.3‰ (solid content). A drop of suspension (approximately 0.2 ml) taken out of the suspension was dropped onto the center of the fused silica substrate. Then, the alcohol began to spread gently on the substrate. The spheres had chances to contact with each other during spreading process. Finally, only the spheres were left on the substrate after the alcohol was removed by spinning (2000 rpm). The substrate was carefully cleaned before it was used, and it is observed by dark field microscope that there were only 0–5 particles per square millimeter after it was cleaned; the contact angle between the alcohol and the cleaned substrate is zero.

The surface roughness could reduce the adhesion force [27], but I cannot find a method to determine the roughness of polystyrene spheres. It is really an uncertain factor, which need further investigation.

The samples were kept in the cabinet at 25 °C and 35% RH for two weeks in order to ensure that some contacted spheres reached the force balance.

The contact radii of the polystyrene particles were determined with a field emission scanning electron microscope (FE-SEM, JEOL JSM-6701F, Japan). In order to eliminate charging-up effect for the insulating material, the samples were coated with a 4-nm-thick layer of Pt by sputtering with the argon at 2.5 kV, 10 mA for 30 s.

3. Results and discussion

Fig. 1 shows the contact between polystyrene spheres with similar size. The polystyrene particles generated the deformation. The reduced radius (defined in Eq. (3)) ranges from 15 nm to 150 nm. The sphericity of particles has a great influence on the correctness of this research. The maximum deviation from the average diameter is less than 1.0%, which implies that the particles have excellent sphericity.

Rimai group extensively did great work on the adhesion of particles to substrates due to surface forces [17–20]. They successfully designed an elaborate experimental process and perfect discussion mode on this subject. Here, we follow their research mode to discuss our results. As a complement to Rimai's method, we also discuss our experimental results in light of theoretical predictions of Du [11].

A log–log plot between the contact radius a and the reduced radius of polystyrene particle R is illustrated in Fig. 2. The unit of the contact radius a and the reduced radius of polystyrene particle R is the nanometer. The size of polystyrene particles ranges from 60 nm to

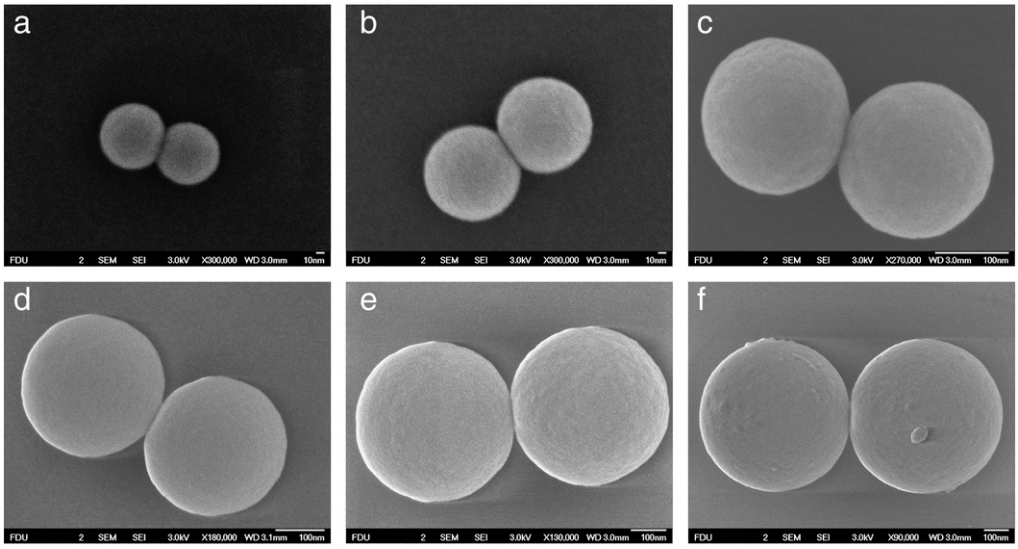

Fig. 1. Contact between polystyrene spheres with similar size. The two polystyrene particles with the reduced radius of (a) 18 nm, (b) 28 nm, (c) 50 nm, (d) 69 nm, (e) 111 nm, (f) 155 nm generated deformation.

600 nm. The contact radii were corrected for the effect of the Pt coating according to Rimai's description [17]. The least-squares-fit line (Fig. 2) reveals that the power-law dependence between the contact radius a and the reduced radius of polystyrene particles R is 0.55 ± 0.04 with a 95% confidence internal. It is not consistent with the JKR or the DMT theory which assumed the elastic deformation and predicted the 2/3 power dependence between the particles. However, it is in reasonable agreement with the MP model which assumed the plastic deformation and predicted the 1/2 power dependence. Thus, polystyrene particles may undergo the plastic deformation due to the surface force.

We testify the correctness of MP model for our experimental data from the aspect of the adhesion work. The mechanical properties of polystyrene spheres used below are published values by Rimai group. Poisson's ratio is 0.38 [28], Young's modulus is 3 GPa and yield stress is 9 MPa [29]. Assuming the occurrence of plastic deformation, the work of adhesion can be calculated using Eq. (1) from the MP model. As shown in Fig. 3, the least-squares-fit line has a slope of 2.9 ± 0.2, the intercept is -2.3 ± 1.4. The work of adhesion calculated from the slope of the curve is 0.106 J/m^2. This is a reasonable value for this system. Moreover, the least-squares-fit line through the points also intercepts the origin within experimental error. This implies the absence of any externally applied load. Similarly, assuming the occurrence of elastic deformations, the work of adhesion can also be calculated by the models of elastic deformation. Assuming the occurrence of elastic deformation, take a 50 nm-sized sphere with a contact radius of 15.8 nm as an example, the work of adhesion, calculated from JKR model and DMT model, is 0.20 J/m^2 and 0.59 J/m^2, respectively. The surface energy of the polystyrene particle is 0.045 J/m^2 [29]. Because the work of adhesion is simply the sum of the surface energies of the two contacting materials minus the interfacial energy (as shown in Eq. (4)), and their interfacial energy is zero, the work of adhesion of two contacting polystyrene spheres is 0.09 J/m^2. Thus, 0.20 J/m^2 is unrealistically large; 0.59 J/m^2 is even more unrealistic. Thus, JKR and DMT models are not applicable to this system. The value of 0.106 J/m^2 (calculated by the MP model) is close to 0.09 J/m^2. The work of adhesion calculated by MP, JKR, and DMT models is listed in Table 1. These results lend further strength to the argument that plastic deformations may occur.

To determine whether the stresses are sufficiently large to cause plastic deformations of the polystyrene particles, it is worthwhile to estimate the average pressure exerted by the adhesion force between the polystyrene particles. The pressure P exerted by the particles on the contact area can be estimated by [30]

$$P = \frac{2w_a}{z_0}. \tag{10}$$

Substituting the experimentally obtained value of the work of adhesion for polystyrene particles, the pressure P is found to be 5.3×10^8 N/m^2. It is larger than the hardness of polystyrene ($2.52 \times$

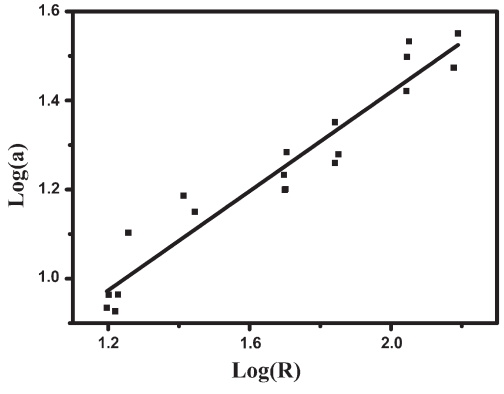

Fig. 2. A log–log plot between the contact radius a and the reduced radius of a polystyrene particle R.

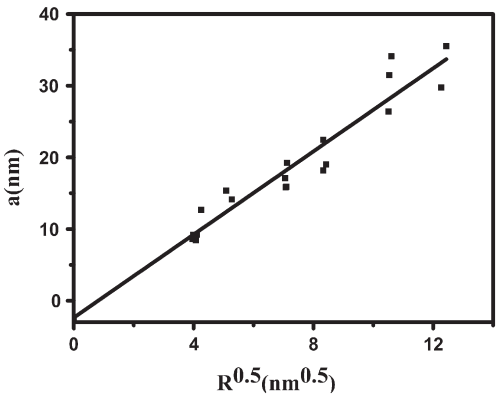

Fig. 3. The linear relation between the contact radius a and $R^{0.5}$.

Table 1
The work of adhesion calculated by MP, JKR, and DMT models.

Model	MP	JKR	DMT
w_a (J/m^2)	0.106	0.20	0.59

10^7 N/m^2 [28]). Therefore, full plastic deformation occurred for the polystyrene spheres in the size range of 60–600 nm.

Du model [11] is also used to determine if the polystyrene particles underwent fully plastic deformation. Kadin et al. argued that higher value of the plasticity parameter S or the maximum approach combined with low values of the Tabor parameter μ results in more intensive plastic deformation [12]. Using Eqs. (6) and (9), the Tabor parameter and the plasticity parameter are calculated, respectively. It is found that $\mu = 0.95$–2.05 ($R^* = 15$–150 nm), $S = 10.5$. In our experiment, the Tabor parameter μ is small, and the plasticity parameter S is much larger than 1, which means fully plastic deformation did occur for the polystyrene spheres in the size range of 60–600 nm.

Therefore, plastic deformation did occur for the contacted polystyrene spheres in the size range of 60–600 nm.

It should be noted that it has been found out that polystyrene spheres in contact with silicon substrates underwent plastic deformation [29], and here, the effect of the interaction of the spheres with the substrate on particle–particle interaction is not discussed, which needs further investigation.

4. Conclusions

In summary, an experiment was conducted to make the polystyrene sphere in the size range of 60–600 nm in contact with the one with the similar size. It was found that the polystyrene sphere deformed due to the surface force. The contact radius varies as the reduced radius to the 0.55 ± 0.04 power, which shows reasonable agreement with the MP theory. Moreover, the calculated plasticity parameter S is much larger than 1, the Tabor parameter μ is small. These all suggest that the polystyrene spheres underwent plastic deformation rather than elastic deformation.

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