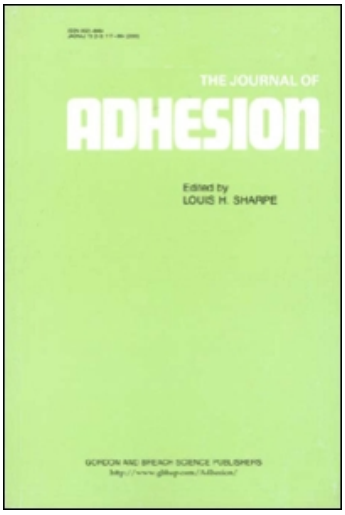

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Time-Dependence of the Adhesion of Micrometer-Size Particles to Substrates: Correlation with Postdeposition Particle Rotation

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Time-Dependence of the Adhesion of Micrometer-Size Particles to Substrates: Correlation with Postdeposition Particle Rotation

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The time dependence of the detachment force of 7-μm ground polyester particles coated with silica nanoparticles from a ceramer-coated substrate was determined by ultracentrifugation. The detachment force of the particles from the substrate was found to increase with the time since the particle deposition. Scanning electron microscopy (SEM) results show that, following deposition, the particles rotate at approximately the same scale as the observed increase in the detachment force. This suggests that the increase in adhesion may be due to particle rotation from their initial positions obtained upon deposition to a more stable position that results from torques generated by either electrostatic or van der Waals forces acting on the particles.

Keywords: Adhesion; Asperities; Fuller–Tabor; Nanoclusters; Particle; Rotation

INTRODUCTION

The respective roles of surface asperities and the dependence of the contact time between a particle and a substrate on the force needed to detach that particle from the substrate have long been of interest [1–8]. In particular, it has been found that the force needed to remove a particle from a substrate often increases with time over periods ranging from days to months. This increase has generally been associated with the occurrence of either plastic or viscoelastic deformation of at

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least one of the materials in contact. In addition, deviations from perfect sphericity have also been shown to decrease the detachment force from that predicted by JKR theory [3,9,10].

The adhesion of real particles to a substrate is far more complicated than an ideal spherical particle or even those that simulate real particles by allowing moderate deviations from sphericity by allowing specified size distributions of asperities. For example, real particles are often the result of a grinding process, are highly irregular, and have asperities that vary in size and shape and are randomly located on the fractured surface of the particles. Under such circumstances, the contact between the particle and the substrate may be established partially through the asperities and partially through the bulk of the particle surface contacting the substrate [11]. The process is further complicated by the fact that particles are generally electrostatically charged and interact with the substrate by both van der Waals and electrostatic interactions. The irregular shape and possible distribution of charge over the surface of the particle can give rise to dipole moments that further complicate the adhesion of particles to substrates [12,13]. In a recent paper [14], Dejesus *et al*. reported an increase in the detachment force of ground polyester particles that had a diameter of approximately 7 μm and had been overcoated with nanometer-size silica clusters from a ceramer-overcoated substrate. This increase occurred over a period of hours, which is much shorter than the previously reported increases in adhesion due to plastic or viscoelastic deformations. The increase was attributed to the rotation of the particle on the substrate subsequent to the initial deposition. In this article, we report the effect of the substrate Young's modulus on the rate of increase in the detachment force. In addition, we more graphically display the rotation of the particles that is coincident with the observed increase in the detachment force.

EXPERIMENTAL

The time dependence of the detachment force between micrometer-size, irregularly shaped polyester particles and a ceramer-overcoated nickelized polyethylene terephthalate (PET) substrate was measured using ultracentrifugation. Particle orientation, position, and possible engulfment on the substrate were determined using scanning electron microscopy (SEM).

The particles used in this investigation comprised ground polyester with mass density of 1.2 g/cm^3 and Young's modulus of approximately 3 GPa [15]. After grinding, the particles were classified by size. The resulting particles had a median number averaged diameter of

approximately 7.0 μm, as measured with a Coulter Multisizer (Beckman-Coulter, Fullerton, CA, USA). The polyester particles were subsequently coated with 1.2 wt.% of silica (Degussa R972, Rockaway, NJ, USA). According to the manufacturer's specifications, the fundamental particle diameter of the silica particles is approximately 7 nm; however, the silica agglomerates into particles having diameter approximately 200 nm as determined by SEM [16].

The substrate comprised a ceramer coating that had been cast on a nickelized polyethylene terephthalate (PET) support. The ceramer was a reaction product of a polyurethane having terminal reactive alkoxysilane with tetraethyl orthosilicate (TEOS). After curing, the coating consisted of a hybrid organic–inorganic network containing 42.2 wt.% of the inorganic phase, as determined by thermogravimetric analysis (TGA). The thickness of the resulting ceramer coating was 18 μm. The molecular weight of the organic phase of the ceramer was 46.8 kg/mol, as determined by size exclusion chromatography (SEC) of the alkoxysilane-terminated polyurethane solution.

The surface energy of the ceramer was determined by measuring the contact angle of droplets of distilled water and diiodomethane and found to be 30 mJ/m^2, with the interfacial energy estimated using the Good–Girifalco approximation [17]. By comparison, the surface energy of the ceramer using in the previous study was found to be approximately 32 mJ/m^2 [14].

The Young's modulus of the ceramer was determined using an Instron Tensile Tester (Instron, Norwood, MA, USA) by measuring the slope of the stress–strain curve and extrapolating to zero stress. The Young's modulus, averaged over six samples, was found to be 2019 ± 204 MPa. By comparison, the Young's modulus of the ceramer used in the previous study was 848 ± 66 MPa [14].

The polyester particles used in this study were the same as those used previously [11,14]. As in the previous studies, the particles were electrostatically deposited onto the substrate using the method of Miskinis [18]. The charge-to-mass ratio of the particles was found to be approximately -30 μC/g, as determined by the method described by Maher [19].

The detachment force measurements were made using ultracentrifugation. The centrifuge was a Beckman LM-70. Ultracentrifuge (Beckman-Coulter, Fullerton, CA, USA) capable of speeds up to 70,000 RPM and having a rotor with a radius of 6.45 cm. The ceramer-coated substrate containing the polyester particles was cut into rectangular strips, and the initial number of particles on five areas was counted using an optical microscope and Image-Pro software (Media Cybernetics, Silver Spring, MD, USA). Typically, there would be between 300 and 400 particles within a given viewing area, and the standard

deviation between the five areas would be less than approximately 20 particles, or approximately 5–8%. The sample was then mounted on appropriate holders that were inserted into the rotor of the centrifuge. The centrifuge chamber was then evacuated to approximately 10^{-5} Torr, and the sample spun was at a selected speed. After spinning, the sample was removed from the centrifuge, and the number of particles remaining was again determined. The centrifuge speeds were randomly selected to eliminate systematic error. The detachment force was defined as the force needed to remove 50% of the particles from the substrate. At the point of detachment, the standard deviation in the count would be approximately 10 particles. The resulting error in the detachment force measurement would be less than approximately 11%. The detachment force measurement as described was repeated after 4, 8, 24, 32, 52, and 72 h from the initial time of deposition of particles on the substrate.

Time-dependent movement of the particles was investigated using SEM. The samples were prepared for SEM analysis using the following procedure. A 1-cm^2 piece of the film with deposited particles was attached to a standard aluminum stub with a double-stick conductive pad. Marker particles were then deposited on the sample by exposing the sample to a gentle air stream with entrained poly(methyl methacrylate) (PMMA) particles. The PMMA marker particles were of uniform distribution and approximately 420 nm in diameter. The samples were then coated with 4 nm of gold to mitigate charging. After the coating was applied, the particles were imaged directly using a Leo 1455 VP electron microscope (Carl Zeiss, Inc., Thornwood, NJ, USA). Images were acquired using an accelerating voltage of 5 keV and a probe current of 50 pA. The sample substrate was tilted to $88^\circ \pm 1^\circ$ with respect to the incoming electron beam.

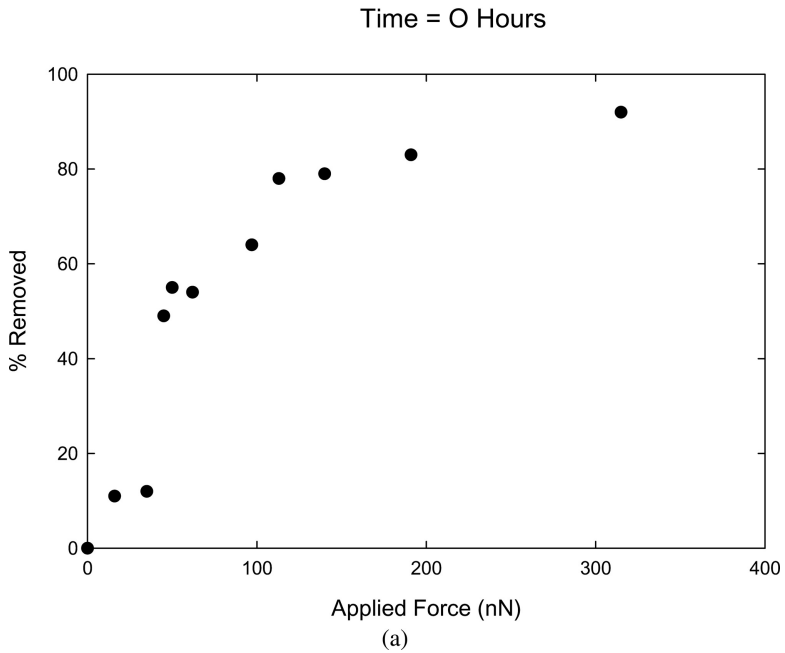
Eight particles were chosen randomly, and each was imaged at times corresponding to the commencement of the detachment force measurements. The particle locations (sample stage positions) were stored by the user interface, providing easy and accurate movement between each particle. The sample was left in the vacuum chamber at the 89° tilt angle for the entire 72 h of the experiment.

To ensure that the apparent rotation of the particles was not due to image distortions arising from charging or other artifact of the SEM, polyester spheres were deposited on a glass cover slip, Au coated, and imaged as described. The three control spheres monitored for 72 h showed identical measurements parallel, perpendicular, and at 45° to the plane of the glass substrate. From these displacements, the uncertainty of the measurements due to imaging factors and sample geometry is estimated as $\pm 5\%$.

RESULTS AND DISCUSSION

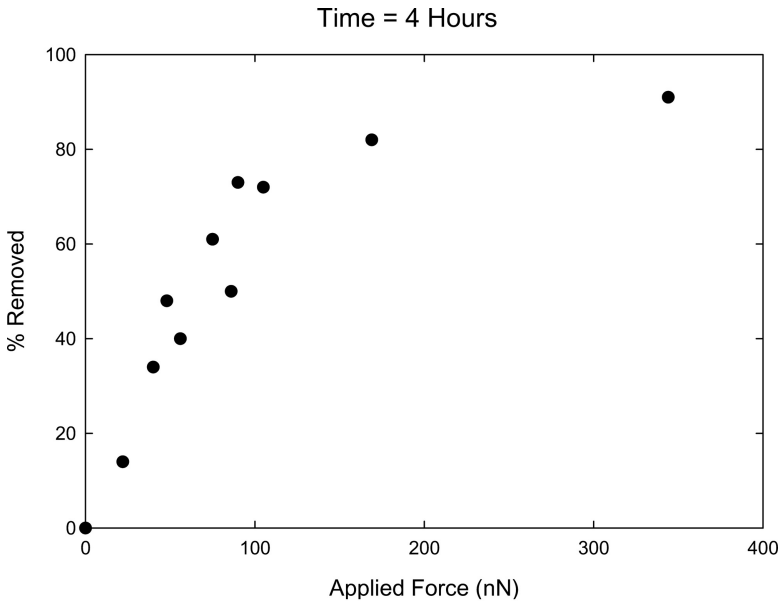
Figures 1a through 1g show the percentage of particles removed from the substrate initially after deposition as well as 4 h, 8 h, 24 h, 32 h, 52 h, and 72 h after deposition. It should be noted that each set of data took approximately 3 h to collect, and so, for example, the particles would have been on the substrate from a few minutes to as much as 3 h to collect the data presented in Figure 1a. However, as previously discussed, the centrifuge speed randomization eliminated any systematic increase in percentage removed at a given applied force during each run.

The percentage of the particles removed can be seen to increase monotonically with increasing applied force for all deposition times. Moreover, by comparing the data in the figures, it is seen that the fraction of the particles that were detached at a given force tended to decrease with increasing time since deposition.

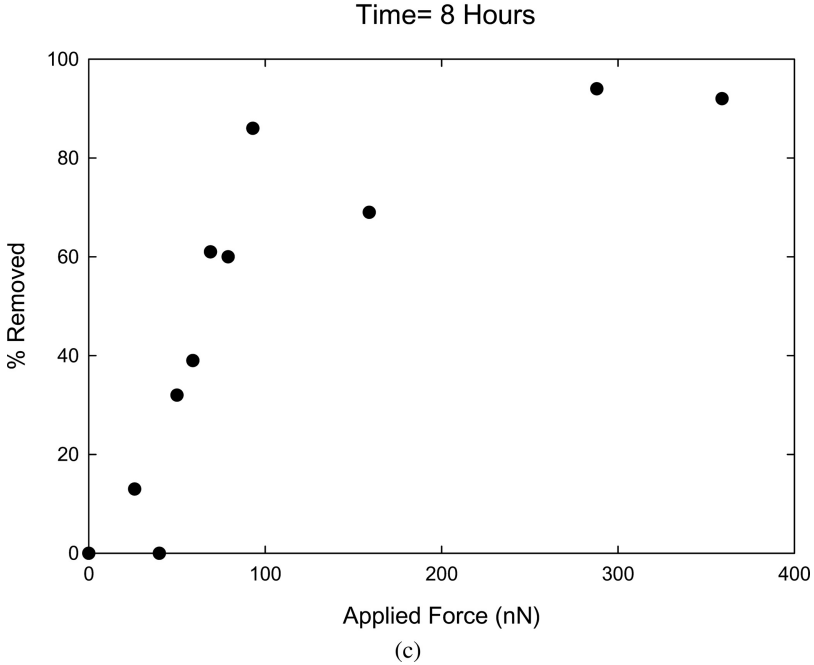


(a)

FIGURE 1 Percent of particles removed as a function of the applied force after initial deposition (a) and after 4 h (b), 8 h (c), 24 h (d), 32 h (e), 52 h (f), and 72 h (g) following deposition.

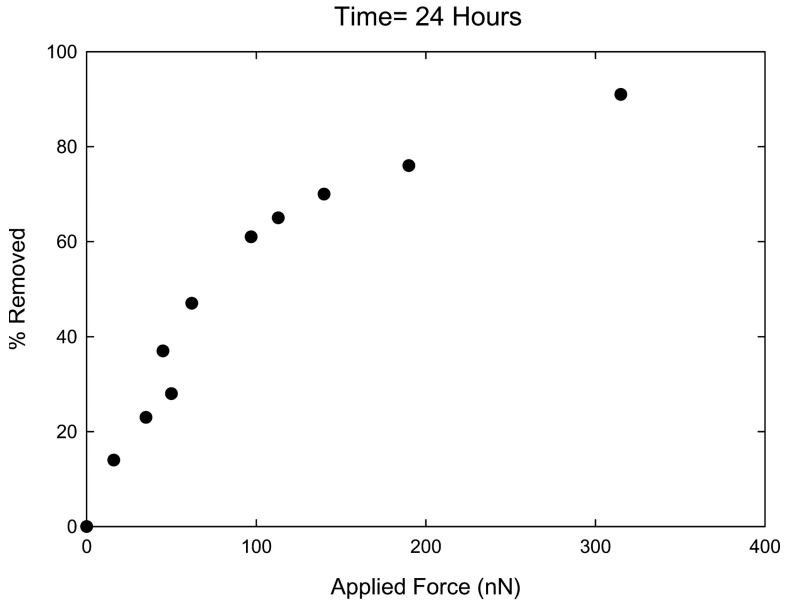


(b)

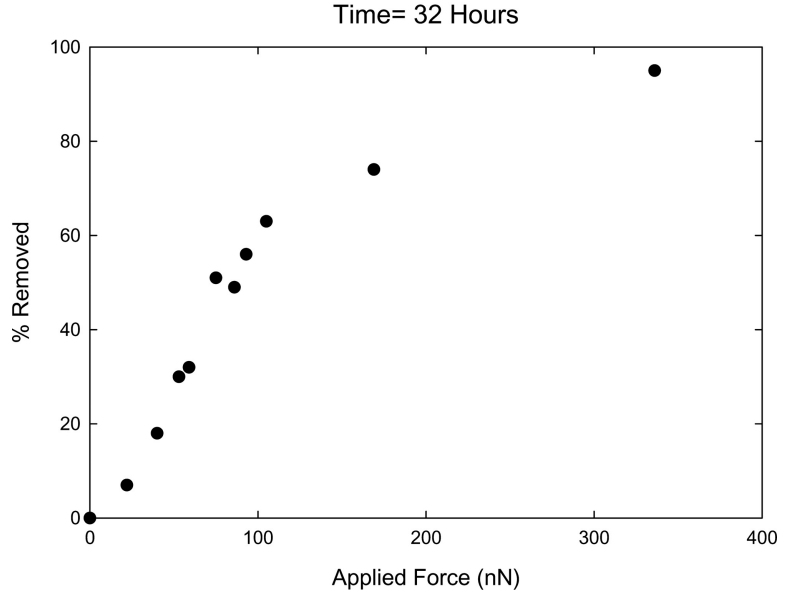


(c)

FIGURE 1 Continued.

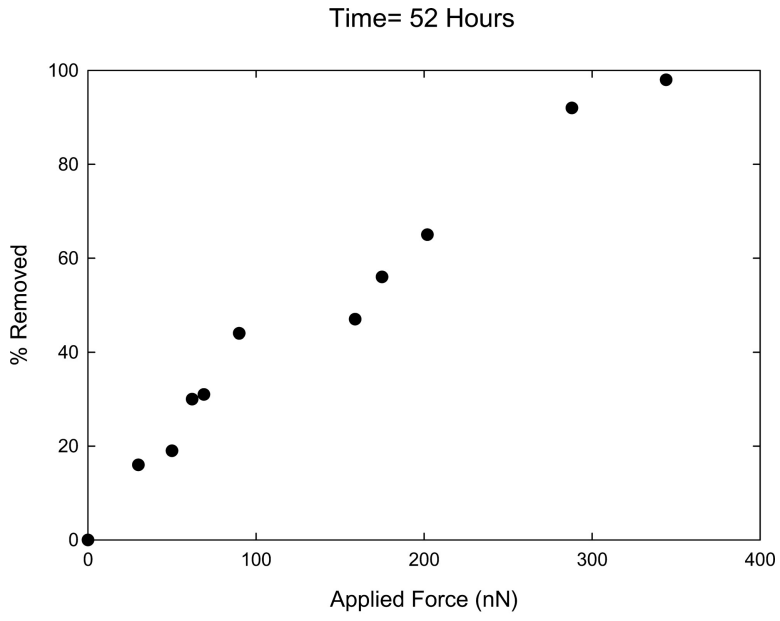


(d)

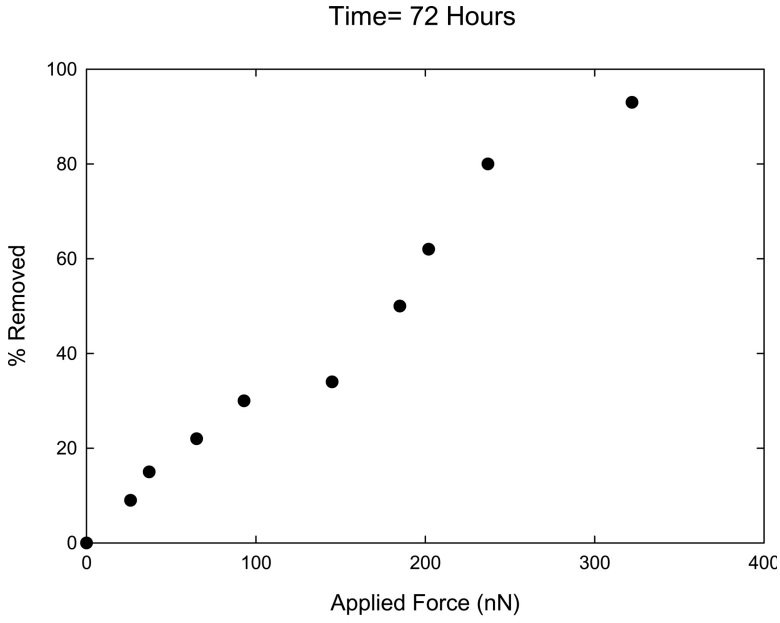


(e)

FIGURE 1 Continued.



(f)



(g)

FIGURE 1 Continued.

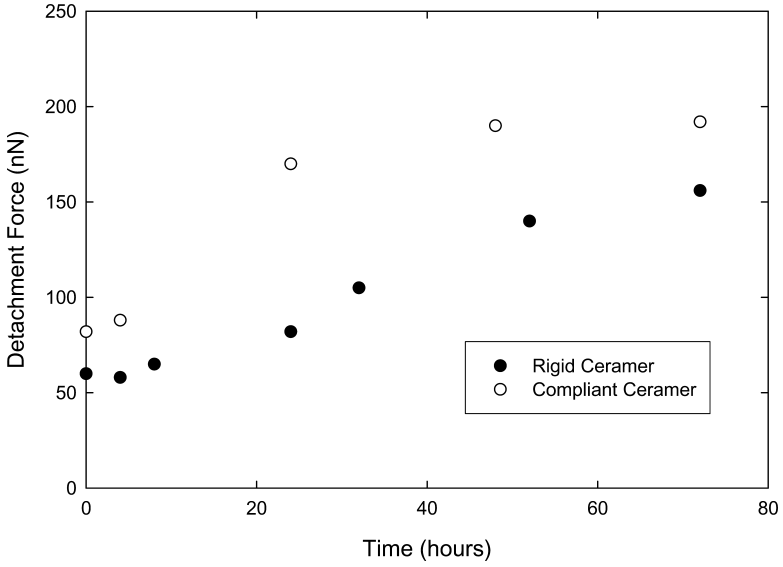


FIGURE 2 Detachment force as a function of time since deposition for particles on the higher and lower Young's moduli ceramers-coated PET substrate. Data for the more compliant ceramer is from Ref. [14].

Figure 2 shows the detachment force as a function of time for both the present (more rigid) and previously reported [14] (more compliant) substrates. Initial values of the detachment force for both substrates are comparable with those reported previously for ceramer substrates with comparable Young's moduli [11]. The detachment force is seen to increase with time, although any variation within the first 4 h is within the limits of error. The lack of significant variation in detachment force over the first 4 h is consistent with the lack of any observed systematic deviation in the percent removed as a function of applied force data obtained during the course of a run. During the first 52 h, however, the force needed to remove the particles from either substrate approximately doubles. After approximately 52 h, the detachment force for the particles on the more compliant substrate appears to asymptotically approach approximately 190–200 nN. There may be a similar trend occurring with the more rigid substrate, but detachment force data going further out in time is needed to determine if this is the case.

One might attempt to ascribe the observed increase in detachment force as a function of time to the occurrence of plastic or viscoelastic deformations. However, this is unlikely, as is illustrated by the SEM micrographs of a particle–substrate contact, taken over a 72-h period,

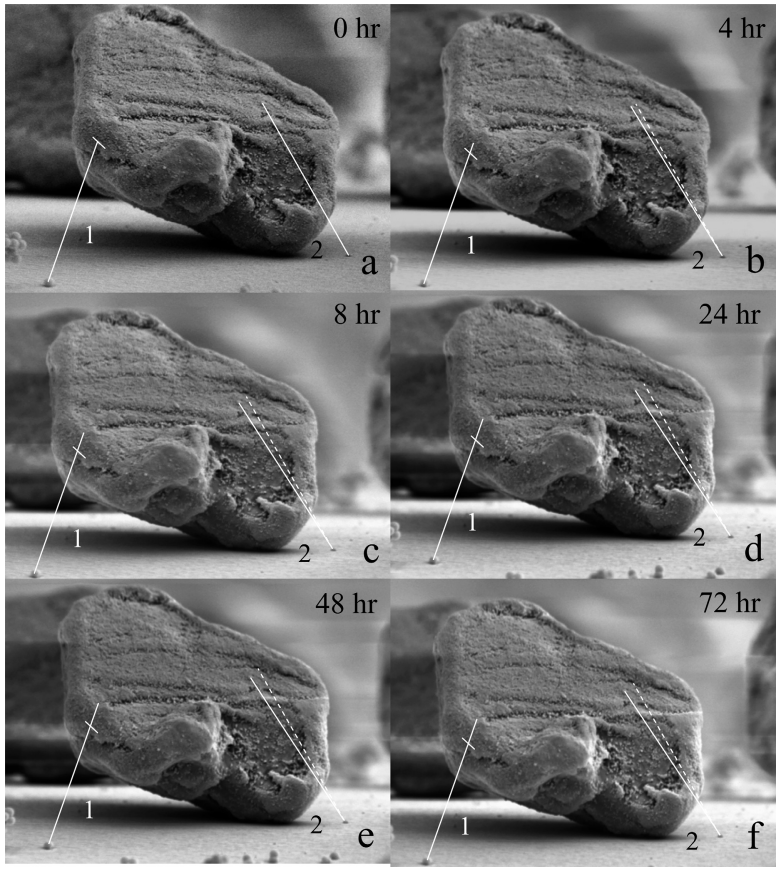


FIGURE 3 Silica-coated polyester particle on ceramer substrate immediately after deposition (a), 4 h after deposition (b), 8 h after deposition (c), 24 h after deposition (d), 48 h after deposition (e), and 72 h after deposition (f).

shown in Figure 3. Specifically, upon close examination of the particle–substrate interface at each time, one finds little evidence of any embedment, after initial contact, of the particle into the substrate. Moreover, the edges of the contact remain sharp and do not show any signs of a meniscus of the substrate around the particle that is indicative of viscoelastic flow [6]. In addition, the smaller PMMA particles do not show any increase in the degree of engulfment with time after the initial embedment. If there were significant plastic flow, it would certainly be expected to be visible with the relatively high stresses associated with the surface interactions between these particles and the substrate. Moreover, although the detachment force is greater

for the polyester particles from the more compliant substrate, the detachment force curves of the particles in contact with the two substrates are approximately parallel, suggesting that the rate of increase in the detachment force is comparable, independent of the Young's modulus of the substrate. Intuitively, one might expect to see some difference in the rate of increase in the detachment force if plasticity were a major factor. Finally, previous studies suggest that plastic deformation becomes significant over a period of days to months [2,6] rather than hours. Although not precluding plasticity as the cause of the increase in the detachment force observed in the present study, these facts suggest that other factors should also be considered. One such factor is the reorientation of the particles on the substrates following deposition.

The increase in the detachment force with time appears to be correlated with the apparent motion or rotation of the particle on the substrate. Specifically, again consider the particle shown in the micrographs in Figure 3, which shows a typical particle on the substrate at times corresponding to those at which the detachment forces were measured.

To track changes in the orientation of the particles, lines were drawn from characteristic markings, such as a particular silica cluster, on each of the eight particles studied in this part of the experiment to PMMA fiducial particles on the substrate. These lines were then copied from the same fiducial particle for each subsequent time. As an example, consider the micrographs of the particle shown in Figures 3a–f. Lines 1 and 2 were drawn on the particle connecting two PMMA particles to distinguishing and trackable markings on the particle. A cross line was drawn across line 1 highlighting the corresponding feature on the particle. The cross line was then kept in the same location on each particle for each subsequent time and line 1 was copied and pasted from the fiducial to the particle, intersecting the cross line. Accordingly, any motion of the particle would show up as a displacement between the end of the line from the fiducial and its intersection with the cross line. A careful examination of line 1 shows that the displacement between the fiducial and the mark on the particle shrinks monotonically with increasing time, although the rate of change decreases after approximately 24 h.

The particle motion tracked with line 2 shows no change in length but rather shows rotation over the same period. This rotation is shown by the pair of lines in Figures 3b–f. In these images, the dashed line is identical to line 2 in panel 3a, whereas the solid line connects the fiducial PMMA particle with the original silica cluster chosen in panel 3a. The angle between the dashed and solid lines increases monotonically

with time. These results are qualitatively similar to those reported earlier for the same particles on a more compliant substrate [14]. Similar variations were observed for all eight particles and can only be ascribed to the movement of the particle on the surface of the substrate following deposition. This movement can be the result of dipole interactions originating from either a nonuniform charge distribution on the surface of the particle, as proposed by Hays [12], or from a uniform charge distribution over the irregularly shaped surface of the particles. Alternatively, the rotation could be the result of surface force interactions along the interface exerting nonuniform stresses along the edge of the contact area between the substrate and the irregularly shaped particle. Further studies are needed to clarify the mechanism(s) that give rise to the tendency of particles to rotate following deposition.

One might attribute the apparent rotation of the particles to the occurrence of plasticity. However, in both this and the previous studies [14], the observed displacement of the particle would have to be accompanied by a readily observed embedment of the particle into the substrate were the rotation simply the result of one or both of the contacting materials deforming. Simply put, the particle would have to significantly deform or embed into the substrate to account for the observed displacement of portions of the particle relative to the substrate. No such distortions were observed in either this or the previous [14] study.

The effect of the rotation of irregularly shaped particles, especially those with particulate addenda, such as the ones used in this study, may be understood in terms of the Fuller–Tabor [5] and/or wedging [11] models. The respective roles of these models on the force needed to detach a particle that is adhered to a planar surface is as follows.

As is well known, the JKR theory [9] predicts that, to remove a particle of radius R from a substrate, a force F_S must be exerted, where F_S is given by

$$F_S = -\frac{3}{2} w_A \pi R, \tag{1}$$

where w_A is the thermodynamic work of adhesion and the minus sign indicates the direction of the force. Upon application of such a force, the contact radius has decreased from a no-load equilibrium value of a_0 to a value $a_S \approx 0.63 a_0$.

However, as is well known, the range of van der Waals interactions is of the order of a few nanometers [20]. Thus, if the surface of the particle and/or substrate is not smooth, the detachment force

should be significantly reduced from that for a spherical particle on a perfectly flat substrate. The effect of surface roughness on adhesion was first modeled by Fuller and Tabor, who assumed that two planar surfaces were separated by asperities that had a Gaussian distribution about a mean diameter r.

Let us first assume that all the asperities were the same size and were all on one surface, the other surface remaining perfectly flat. Under these assumptions, all asperity contacts would have to break simultaneously upon application of an external force of sufficient magnitude, at which point separation would occur. If there were n asperities that separated one surface from the other, the detachment force F_A would then be given by

$$F_A = \frac{3}{2}\pi w_A n r. \tag{2}$$

However, according to the Fuller–Tabor model, F_A actually overestimates the size of the detachment force because, upon application of a sufficient force, the contact between the planar substrate and the smallest of the asperities would break first. The breaking of the smallest asperities would, in effect, determine the force needed to separate the two surfaces. Thus, Equation 2 represents the maximum detachment force allowable under the Fuller–Tabor model.

Although an actual detachment force is difficult to predict from the Fuller–Tabor model, F_A can be estimated in a fairly straightforward manner. Assuming a mass density of the silica of approximately $2\,\mathrm{g/cm^3}$, the number of silica particles per unit surface area of the polyester particle can be calculated from the respective radii of each type of particle and weight percent of the silica. Bowen *et al.* [21] showed that the actual contact between ground particles of similar size and composition and a planar substrate is approximately 5–10% of the cross-sectional area. The number of silica particles in contact with the substrate is estimated to be between 4 and 8. If the work of adhesion is then assumed to be approximately $0.04\,\mathrm{J/m^2}$ [11], one finds that $75\,\mathrm{nN} \leq F_A \leq 150\,\mathrm{nN}$.

It is apparent from the data shown in Figure 2 that the force needed to detach the particles from both the lower and higher modulus substrates is consistent with the predictions of the Fuller–Tabor model although, at the longer times, those values are close to the maximum allowed.

In a recent paper in which the detachment force was determined for these same particles on similar substrates that were more or less compliant, Dejesus *et al.* [11] found that the measured detachment force was, in some instances, greater than that predicted by the

Fuller–Tabor model. Recognizing that the Fuller–Tabor model did not allow for non planar contacts, they proposed that the silica could be serving as wedges that would decrease the contact radius a between the particle and substrate so that $a_S < a < a_0$. The net detachment force would, then, be just that incremental force needed to reduce the contact radius from a to a_S. Either of these mechanisms can, at least qualitatively, account for the increase in adhesion with time. Specifically, upon initial impact, the particle is not in its equilibrium position. Rather, dipole interactions and surface forces rotate the particle until equilibrium is established. This can either increase the number of silica particles contacting the substrate or cause the contact radius to increase as the particle pivots around those silica particles contacting the substrate. Elaboration on the specific mechanism causing the increase is a topic for future research.

Alternatively, one might argue that the silica is becoming plastically engulfed into the substrate with time, thereby causing the observed increase in adhesion. However, if this were the case, one would expect to see some evidence of either the polyester particle beginning to sink into the substrate or, at least, the PMMA particles, which are closer in size to the silica, further embedding into the substrate over the time scale of this study. Neither effect is observed, thereby arguing against the increase due to plastic deformation. One would also expect to see a visible difference in the polyester particle-to-substrate contact because of the macroscopic shift in the orientation of the particle. Again, this was not observed.

This study raises, perhaps, more questions than it answers. It is clear from both this and a related paper [14] that there is an observed increase in the detachment force and a reorientation of the particles subsequent to the deposition. Moreover, both of these effects occur on approximately the same time scale. This makes an interesting correlation but does not prove that the rotation of the particles results in the observed increase in the detachment force. Although it is proposed that the increase in adhesion can be explained in terms of the Fuller–Tabor model, taking into account additional contacts between either the silica or the polyester particle and the substrate, and that arguments can be made against the occurrence of plasticity, neither proposal has been unequivocally proven.

The rotation of the particles is another area where further research can be conducted. Obviously, it is necessary to demonstrate whether the rotation is directly related to the increase in adhesion. It is also worthwhile to determine the forces giving rise to the rotation and to understand why the rotation occurs with a time scale of tens of hours rather than instantaneously. It is clear that there is much research

that needs to be done both experimentally and theoretically to understand these results.

CONCLUSIONS

The detachment force of silica-coated, ground, micrometer-size polyester particles from ceramer-overcoated nickelized PET substrates was found to increase with the time since deposition, although the rate of increase may decrease after approximately 52 h. The magnitude of the detachment force is greater from the ceramer with the lower Young's modulus. The magnitude of the detachment force is consistent with the predictions of the Fuller–Tabor asperity and the Dejesus wedging models. The time dependence of the detachment force correlates temporarily with the rotation of the particles on the substrate after deposition.

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