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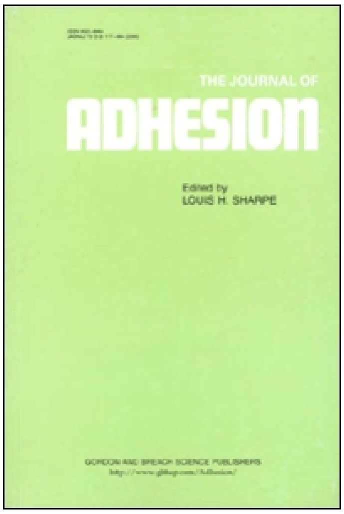

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The Adhesion of Particles to Polymer Coated Substrates

D. S. Rimai[a]; L. P. Demejo[a]; R. C. Bowen[b]

[a] Office Imaging Research and Technology Development, Eastman Kodak Company, Rochester, NY, USA [b] Analytic Technologies Division Research Laboratories, Eastman Kodak Company, Rochester, NY, USA

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The Adhesion of Particles to Polymer Coated Substrates*

D. S. RIMAI** and L. P. DEMEJO

Office Imaging Research and Technology Development, Eastman Kodak Company, Rochester, NY 14653, USA

and

R. C. BOWEN

Analytic Technologies Division Research Laboratories, Eastman Kodak Company, Rochester, NY 14650, USA

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A rigid polyester substrate was overcoated with 10 μm, 25 μm, and 50 μm thick coatings of polystyrene containing varying concentrations of plasticizer between 0% and 20%. Micrometer-size glass spheres were deposited onto these substrates and the deformations of the substrates resulting from the forces of adhesion were then examined using scanning electron microscopy (SEM). For substrates which were in the glassy phase, the power law dependence of the contact radius on particle radius was 0.48. In contrast, for the case of rubbery substrates, the contact radius was found to vary as the particle radius to the 0.65 power. These results are consistent with the predictions of the adhesion models of Maugis and Pollock [D. Maugis and H. M. Pollock, *Acta Metall.* **32**, 1323 (1984) and Johnson *et al.*, [K. L. Johnson, K. Kendall, and A. D. Roberts, *Proc. Roy. Soc. London Ser. A* **324**, 301 (1971)], respectively. This implies that, depending on the glass transition temperature of the substrate, either plastic or elastic deformations can occur. Also presented and discussed is the observation of critical engulfment, whereby the surface forces draw the particle substantially or totally into the substrate.

KEY WORDS adhesion; particle; deformation; embedding; JKR; work of adhesion; polymer; coating; plasticizer; engulfment.

INTRODUCTION

The adhesion of particles to surfaces has been of interest for over 60 years. The stresses resulting from the surface forces can result in a deformation occuring between the contacting materials, as originally postulated, independently, by Bradley,[1,2] and Derjaguin.[3] In effect, then, the adhesion of a particle to a surface is a combination of surface energetics and mechanical responses of the materials to the surface-force-generated stresses.

Polymers are frequently coated onto substrates in order to affect adhesion. In some instances, such as with adhesive tape, the role of the polymer is to increase

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** Corresponding author

adhesion. Alternatively, paints are formulated to facilitate surface cleaning. Other areas where polymers have been coated onto various substrates in order to control adhesion include xerography, magnetic discs, and of course, cooking utensils.

In this paper, measurements of the adhesion-induced contact radius between glass particles having nominal radii of 4 μm and 11 μm, in contact with plasticized polystyrene coatings, are reported. There are several reasons for conducting such studies. Firstly, the information extracted is important scientifically and technologically. Secondly, by using particles in this size range, much can be learned about adhesion, in general, without having extraneous complications arising from other types of interactions. For example, consider a spherical particle with a radius of 10 μm that is uniformly charged to the field emission limit. If this particle is placed on a 10 μm thick polymeric coating over a metallic support, the electrostatic force of attraction due to the image charge (ignoring polarization effects of the particle and coating) would be an order of magnitude less than the van der Waals interactions. Gravitational forces on such a particle would be negligible. Moreover, such differences increase with decreasing particle size.

In addition to adhesion forces, such as those arising from van der Waals interactions, being the dominant mode of interaction for small particles, adhesion effects can be studied at equilibrium by examining the particle-substrate contact area. There is no need to separate materials, as would have to be done if one were to use calorimetry or a surface force apparatus.[4] Moreover, once the nature of the deformation has been determined, it is frequently possible to determine the work of adhesion between the contacting solids. Finally, as previously discussed, adhesion properties depend on both the surface energetics and the mechanical response of the system. This technique allows studying adhesion as an integrated process, rather than from just a surface energetics viewpoint.

BACKGROUND

Derjaguin first attempted to calculate the contact radius between a particle and a substrate.[3] He assumed that the particle could be treated as a Hertzian indentor so that the contact radius, a, would be related to the initial (undeformed) loading force, F^0, particle radius, R, and the Young's modulus, E, and Poisson's ratio, ν, of the substrate by

$$a^3 = \frac{3}{4} F^0 \left[\frac{1-\nu^2}{E} \right] R \tag{1}$$

He further assumed that the loading force was due to van der Waals interactions,[5] so that

$$F^0 = \frac{\hbar\bar{\omega}}{8\pi z_0^2} R \tag{2}$$

where $\hbar\bar{\omega}$ is the Hamaker coefficient and z_0 is the separation distance between the two materials (approximately 4 Å for van der Waals bonded crystals). Upon substitution of Equation (2) into Equation (1), Derjaguin calculated that

$$a^3 = \frac{3\hbar\bar{\omega}}{32\pi z_0^2}\left[\frac{(1-\nu^2)}{E}\right]R^2 \tag{3}$$

While studying the interactions between homologous combinations of macroscopic gelatin and rubber spheres, Johnson *et al.* found that the experimentally-determined contact radius was approximately twice that predicted by the Derjaguin model.[6] (Later studies[7] showed that the disagreement is even greater for micrometer-size particles). To account for this discrepancy, they proposed a theory (hereafter referred to as the JKR model) which proposed that particle-surface interactions could not be treated as a simple Hertzian indentor. Rather, there existed a mutual attraction which resulted in compressive interactions towards the center of the contact zone and tensile interactions towards the outer regions of this area. According to the JKR model, both types of interactions contribute to the size of the radius of contact and the contact radius is related to the particle radius, the thermodynamic work of adhesion, w_A, and any externally applied load, P, by

$$a^3 = \frac{R}{K}\{P + 3w_A\pi R + [6w_A\pi RP + (3w_A\pi R)^2]^{1/2}\} \tag{4}$$

where w_A is related to the surface energies of the two materials, γ_1 and γ_2, and their interfacial energy, γ_{12} by

$$w_A = \gamma_1 + \gamma_2 - \gamma_{12} \tag{5}$$

and

$$K = \tfrac{4}{3}\pi(k_1 + k_2) \tag{6}$$

where

$$k_i = (1-\nu^2)/E_i \tag{7}$$

and ν_i and E_i designate the Poisson ratio and Young's modulus of the i^{th} material. If one material is relatively non-compliant compared with the other, as is the case in this study where results pertaining to rigid particles on compliant substrates are presented, and there were no adhesion, Equation (4) reduces to Equation (1). Alternatively, if the particle is not subjected to any external load, the JKR model predicts that

$$a^3 = \frac{9w_A\pi R^2(1-\nu^2)}{2E} \tag{8}$$

Finally, owing to the requirement that the roots of the radical in Equation (4) must be real, the JKR theory predicts that, upon application of a negative load, the particle would separate when the force, P_s, equals

$$P_s = -\tfrac{3}{2}w_A\pi R \tag{9}$$

Moreover, separation would occur at a finite contact raidus, a_s, which would equal approximately 0.63 of the contact radius under no load conditions. It should be noted that P_s does not depend on the Young's modulus of the materials according to the JKR model. This, of course, is contrary to many everday experiences. Pressure sensitive adhesives generally consist of moderately low surface energy (approximately 0.035 J/m^2), highly viscoelastic elastomers. Finally, the adhesion of particles to elastomers is known to depend upon the elastic modulus to the elastomer. The resolution of this discrepancy is related to hysteretic effects experienced by materials during loading and unloading cycles. This topic is discussed in more detail elsewhere[8,9] and is beyond the scope of this paper.

The adhesion-induced stresses involving polymeric materials can be of the order of 10^8–10^9 Pa,[10,11] which is comparable with the Young's modulus of typical thermoplastic materials and far above their yield strengths.[12] Under such circumstances, at least one of the contacting materials can yield, thereby resulting in a plastic deformation. The significance of such a deformation is that, whereas much energy is recovered upon the removal of a particle from a substrate in the case of elastic deformations (the so-called "elastic rebound effect"[5]), a large amount of the energy going into creating a plastic deformation is lost.

The occurrence of plastic deformations resulting from forces of adhesion was first postulated by Krupp.[5] He proposed a phenomenological model wherein the contact zone could be divided into two regions: an inner, high stress, circular region which would deform plastically, and an outer, low stress, annular region which would deform elastically. His model utilized a time-dependent hardness to allow for plasticity and assumed that only compressive stresses existed.

More recently, Maugis and Pollock[13] extended the JKR model to include the case where the stresses due to the forces of adhesion cause a plastic deformation. According to their model, the contact radius depends upon a material's hardness, H, which is three times the yield strength, Y, of the material, according to the relationship

$$P + 2\pi w_A R = \pi a^2 H \tag{10}$$

In the absence of any externally applied load, Equation (10) reduces to

$$a = [2W_A R/3Y]^{1/2} \tag{11}$$

where the yield strength, Y, equals 1/3 H. For a typical thermoplastic Y is approximately 0.3% of its Young's modulus.[12]

EXPERIMENT

A linear styrene butylacrylate copolymer, produced from monomers in a ratio by weight of 70:30, was plasticized by blending with Eastman Kodak Santicizer 261^{TM} in varying amounts ranging from 0% to 20%, dissolved in dichloromethane, and coated onto an Estar^{TM} support. In general, the coatings were 10 μm thick. Additional coatings having thicknesses of 25 μm and 50 μm of the material containing

20% plasticizer were also made. Scanning electron microraphs of the cross sections of the polymer coatings showed no contrast variations due to differences in the emission of secondary electrons, suggesting the absence of any phase separation between the styrene butylacrylate and the plasticizer. As discussed by van Krevelen,[11] the addition of plasticizer to a polymer reduces the polymer's glass transition temperature (T_g). For the styrene butylacrylate used in this study, the T_g decreased linearly with increasing plasticizer concentration from approximately 52°C for the sample with no plasticizier to 0°C for the sample with 20% plasticizer, as measured using differential scanning calorimetry (DSC).

As is well known,[12] amorphous polymers have four distinct rheological regions. At temperatures below T_g the polymer is glassy and has a Young's modulus of approximately 3 GPa. When the temperature is approximately equal to T_g, the polymer enters the transition, or leathery, zone. In this region the Young's modulus decreases by approximately three orders of magnitude within a temperature change of a few degrees Celsius. With a further increase in temperature, the polymer enters the rubbery or plateau region. Here, the polymer acts as an elastomer and typically has a Young's modulus of the order of 3×10^6 Pa. Finally, as the temperature is increased, the polymer enters the terminal region. At this point the Young's modulus again decreases rapidly with increasing temperature and the polymer appears to be "tacky". Although the glass transition temperature varies with material composition, the shape of the rheological curve does not vary significantly. This behavior is approximately independent of chemical composition, molecular weight, cross-link density, etc. and the curves describing the Young's modulus as a function of temperature are known as universal curves. Therefore, if the glass transition temperature of an amorphous polymer is known, its Young's modulus can be closely estimated.

As is also well-known,[12] the principal effect of a plasticizer is to reduce the glass transition temperature of a polymer. Accordingly, if an unplasticized polymer has a glass transition slightly above the ambient temperature, the addition of small amounts of plasticizer can cause the Young's modulus of the polymer to decrease by orders of magnitude as the glass transition is decreased to below room temperature. Moreover, the Young's modulus of the polymer can be closely estimated from the universal curves if the concentration of plasticizer is known.

Direct determination of the mechanical properties, such as Young's modulus and yield strength, of the coatings presented experimental difficulties because the underlying substrate dominated the mechanical response of the system. These properties, in principle, could be measured using the bulk materials. However, entrained solvents, etc. would still alter these properties, particularly for the plasticized materials, from those of the actual coatings. In this study, estimates of the moduli of the coatings were made by using the rheological data of the unplasticized materials and calculating the shift T_g as a function of plasticizer concentration. The moduli were then estimated using the appropriate modulus–temperature universal curves. The estimated glass transition temperatures and Young's modulus at room temperature are given in Table I. These values of modulus corresponded to the following qualitative properties of the coatings. The first two coatings, containing 0% an 5% plasticizer, were quite stiff, suggesting a material that was in its glassy phase. The

TABLE I
Estimated Young's moduli at room temperature and glass transition temperatures of the plasticized styrene butylacrylate copolymer coatings

Percent plasticizer (weight %)	Young's Modulus (Pa)	T_g(°C)
0	3×10^9	52
5	3×10^9	39
10	10^8	26
15	10^7	13
20	10^5	0

10% plasticized coating behaved like a stiff elastomer, suggesting a material in the transition zone. At 15% the coating appeared rubbery. Finally, at 20%, the coating was soft and "sticky", reminiscent of polymers in the terminal rheological phase.

Yield strengths are assumed[12] to be approximately 0.3% of a material's Young's modulus. The precise values of these parameters are important only for calculating accurate values of w_A and do not impact the general observations and conclusions of this paper. Their values are stated so as to give the reader a feeling for the mechanical states of the coatings.

Dry, spherical, glass particles, having nominal radii of 4 μm and 11μm, were obtained from Duke Scientific, Incorporated. There was considerable size variation of the particle size about the mean. These particles were deposited onto the substrate by gently dropping them from a height of less than 1 cm. By using this technique, the impact energy would be insufficient to create contact radii[14–16] of the size observed in this study. The modulus of the glass particles was not measured. However, the modulus of glass is approximately 70 GPa and is large compared with any of the substrates. Any observed deformations would, therefore, be due only to the substrate deforming. After the particles were deposited, the samples were stored in a cabinet under atmospheric conditions, horizontally, for approximately two weeks to allow any stresses to relax. Based on experience with these samples, the storage conditions should not affect the contact radius or encapsulation.

The contact radii were determined using the secondary electron emission from a scanning electron microscope (SEM). To avoid beam-induced charging and to reduce any Joule heating, the samples were first coated with a 10 nm thick 60:40 gold:palladium alloy. This was accomplished by sputtering the alloy with argon for approximately 60 seconds at 2.5 kV and 20 mA, using a Polaron E5100 high- resolution sputter coater. It had previously been found[17] that the temperature rise during the sputtering process was less than 20°C. Although such a temperature rise should not significantly affect the results of this study, any such effects were further reduced by mounting the samples onto a cold stage during the sputtering process. Under these conditions the temperature of the sample during sputtering was approximately 5°C.

The samples were mounted onto cross-sectional stubs to allow viewing at the high tilt angles desired and placed into a Philips 515 SEM. Imaging was accomplished with the beam at an 88° angle to the normal to the plane of the substrate. A 15 kV accelerating voltage and 10 nm beam size were used. Viewing times were kept as short as possible to reduce further any charging and Joule heating effects. Towards this end, each particle and contact radius was determined from a single micrograph. To permit accurate determinations of both radii, particularly on the more rigid substrates, most of the particle was imaged at a relatively low magnification. However, in the vicinity of the contact zone, the magnification would be increased, thereby resulting in a split micrograph. This technique was unnecessary when viewing particles on the more compliant substrate because of the size of the contact radii.

RESULTS

Figure 1 shows nominal 4 μm radius particles on 10 μm thick coatings containing 0% (Figure 1a), 5% (Figure 1b), 10% (Figure 1c), 15% (Figure 1d), and 20% (Figure 1e) plasticizer. Figures 2a through 2e show nominal 11 μm radius particles on the same substrates, respectively. As can be seen by comparing Figure 1a with 1b and 2a with 2b, the contact radius does not significantly vary upon the addition of 5% plasticizer to the polymer coating. This is consistent with the estimation that the addition of this much plasticizer should not reduce the T_g of the coating material to below ambient temperature and, accordingly, the Young's modulus should not significantly change. Moreover, as can be seen from Equations (8) and (10), any effects arising from the slight decrease in Young's modulus or yield strength would be masked by the weak dependence of the contact radius on either of these parameters.

The depth of penetration of the particle into the substrate is also seen to increase with increasing plasticization. In particular, the nominal 4 μm radius particles are seen to become almost submerged when contacting the 20% plasticized polymer. This effect is particularly apparent in the upper left corner of Figure 1e, where a particle appears to be below the surface of the substrate. It should be emphasized that the planes of the substrates are at approximately 90° to the horizontal and the mass of these particles are negligible. Therefore, this effect cannot be due to gravity. Moreover, although the depth of penetration also increases for the larger, more massive, particles, the amount of penetration relative to the size of the particle is less and the engulfment observed with the smaller particles is not observed with the larger ones. Furthermore, the contact radius increases with increasing particle radius for a given substrate, but the increase appears to be at a rate that is less than linear.

In previous studies,[8,10,11] adhesion-induced plastic and elastic deformations of materials were distinguished using the power law dependence of the contact radius on the particle radius. In those studies it was found that glass particles deformed an elastomeric substrate elastically, whereas polystyrene particles, at temperatures below their T_g in contact with polished silicon substrates, deformed plastically. Moreover, for relatively large deformations of a compliant substrate, such as occurs with small particles or extremely low modulus materials, anomalous power law dependences have been found.[8,18,19]

The previous results were obtained on vastly different materials. Moreover, the results suggestive of plastic deformations were obtained with the particles flattening whereas the deformations consistent with elastic theory were obtained with the substrate being penetrated. It is, however, possible to see if such a transition from plastic to elastic deformations occurs in the present case by determining the power law dependence of the contact radius on particle radius with the substrate just below and above its glass transition temperature. This is most readily done using the coatings containing 5% and 10% plasticizer. Figure 3 shows a log-log plot of the contact radius as a function of particle radius for the glass beads on the substrate containing 5% plasticizer. The slope of the least squares fit line is 0.48 with a correlation coefficient

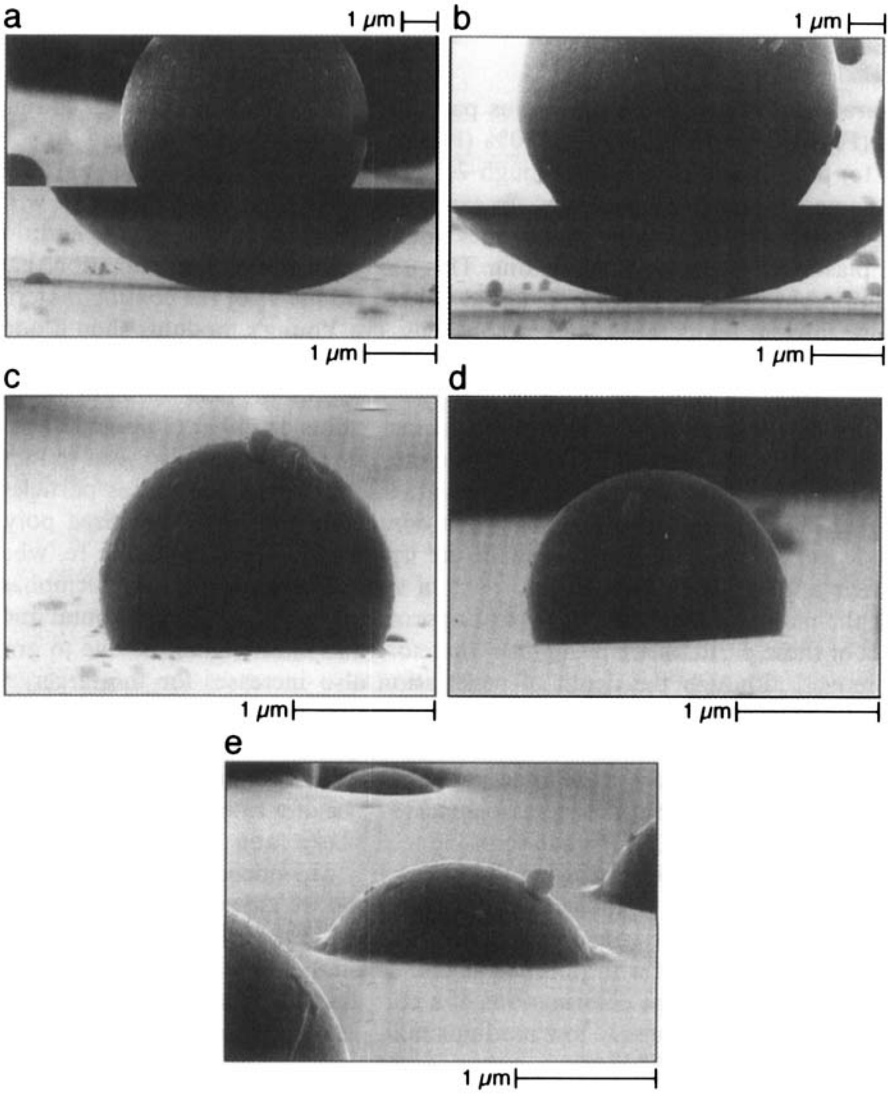

FIGURE 1 Nominal 4 μm radius particles on 10 μm thick coatings containing 0% (Figure 1a), 5% (Figure 1b), 10% (Figure 1c), 15% (Figure 1d), and 20% (Figure 1e) plasticizer.

of 0.96. This result is consistent with the predictions of the Maugis-Pollock theory,[13] expressed by Equation (10). Figure 4 shows a plot of the contact radius as a function of the square root of the particle radius. The extrapolated line is seen to intersect the origin. This suggests that any externally applied loads, such as those due to beam-induced or triboelectric charging or gravity, are small compared with the surface forces.

A similiar analysis was performed for the case where the substrate contained 10% plasticizer. Figure 5 shows a log-log plot of the contact radius as a function of the

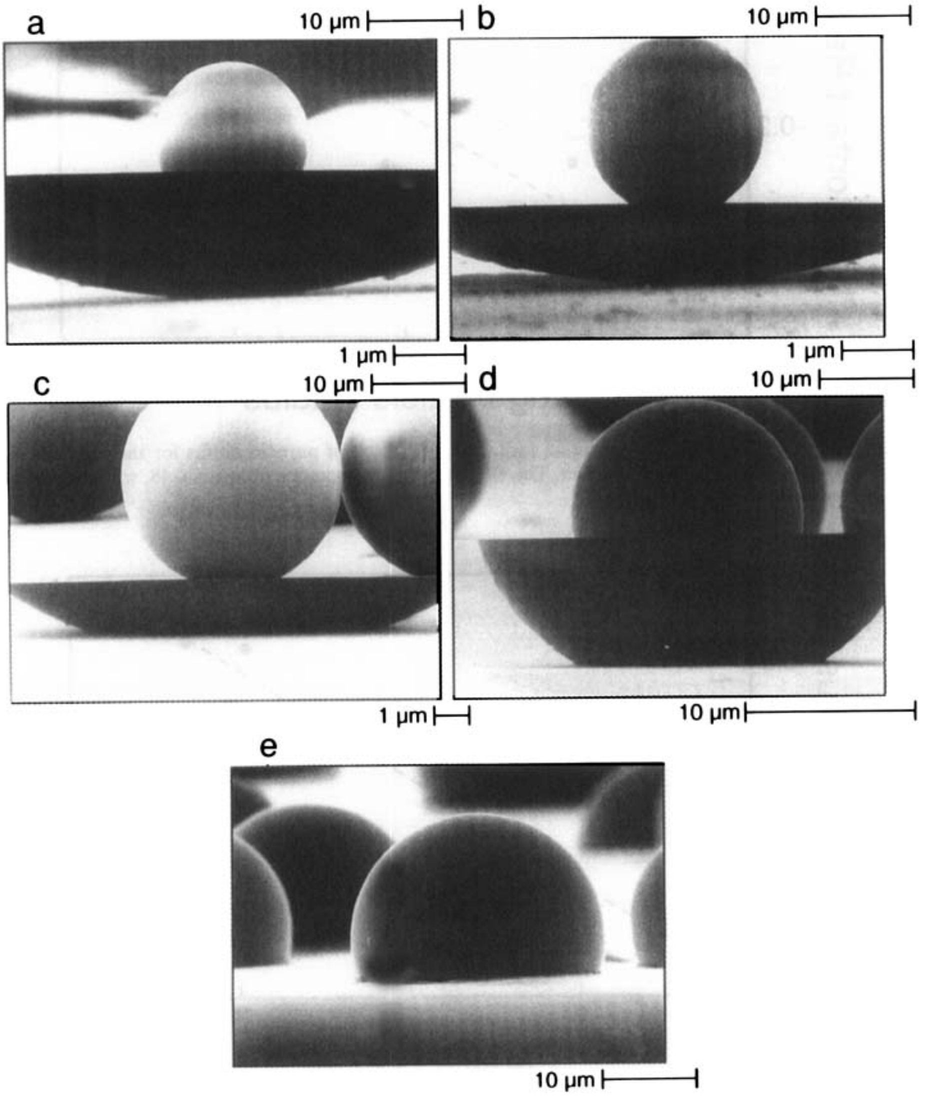

FIGURE 2 Nominal 11 µm radius particles on 10 µm thick coatings containing 0% (Figure 1a), 5% (Figure 1b), 10% (Figure 1c), 15% (Figure 1d), and 20% (Figure 1e) plasticizer.

particle radius for this more highly plasticized substrate. In this instance, the slope of the least squares fit line was found to be 0.65 with a correlation coefficient of 0.97. This result is consistent with the predictions of the JKR model.[6] Figure 6 shows the the contact radius as a function of particle radius to the 2/3 power. As before, the

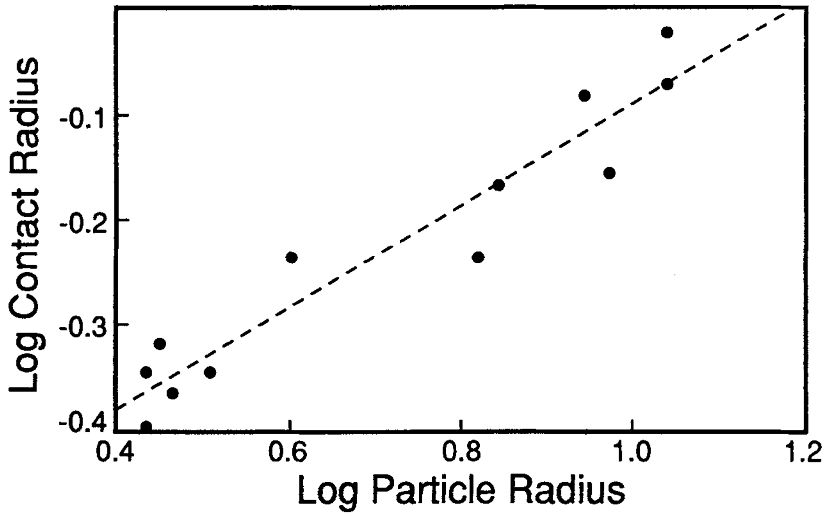

FIGURE 3 A log-log plot of the contact radius as a function of particle radius for the case where the substrate coating contains 5% plasticizer. The slope of the least squares fit line is 0.48, with a correlation coefficient of 0.96.

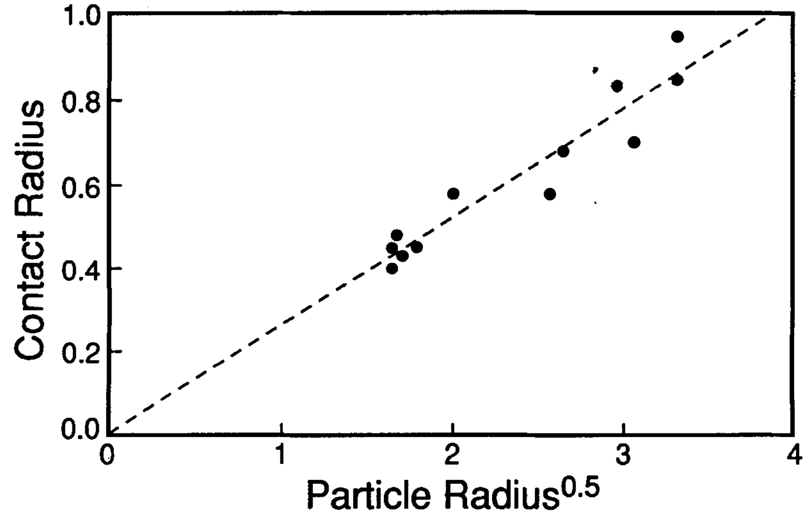

FIGURE 4 A plot of the contact radius as a function of the square root of the particle radius. The least squares fit line through the data is seen to intersect the origin, which suggests the absence of any applied load.

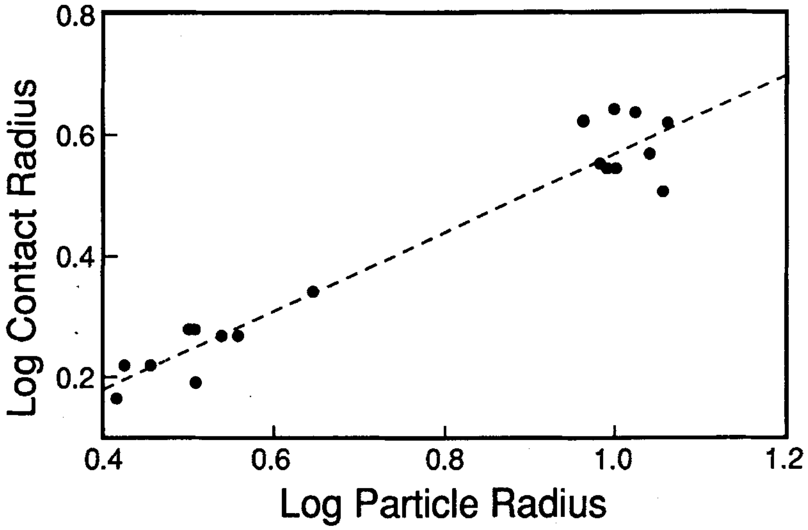

FIGURE 5 A log-log plot of the contact radius as a function of particle radius for the case where the substrate coating contains 10% plasticizer. The slope of the least squares fit line thorugh the data is approximately 0.65, with a correlation coefficient of 0.97.

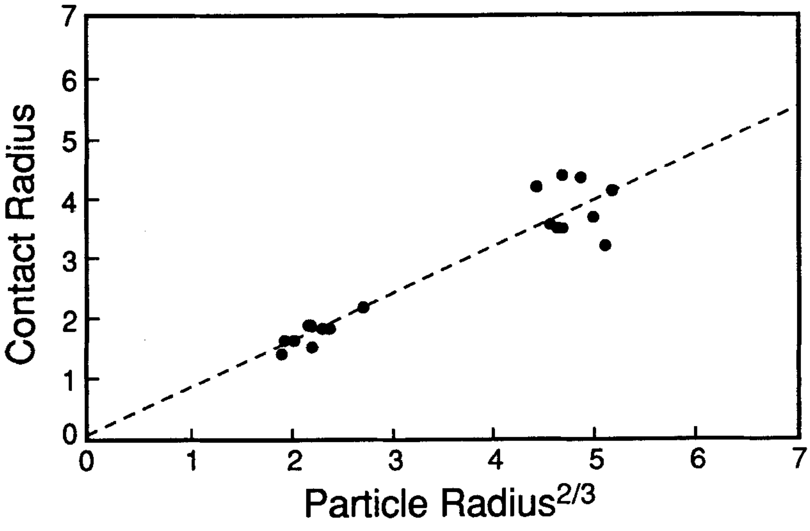

FIGURE 6 A plot of the contact radius as a function of particle radius to the 2/3 power. The extrapolated least squares fit line through the data intersects the origin, suggesting the absence of any significant applied load.

least squares fit line through the data intersects the origin, within the limits of error of the experiment, suggesting the absence of any significant applied load.

It should be emphasized that, in both examples, the particles are the same and the substrates differ only in the amount of plasticizer present. The principal difference between these examples is that, in one instance, the substrate is just below its T_g and is, therefore, in a glassy state, whereas in the other, the substrate is just above its T_g and is in either the transition or rubbery state. The effect on particle adhesion and, specifically, on the contact radius, of having the substrate traverse repeatedly through its glass transition would be an interesting subject for future studies.

In previous studies,[8-11,17-19] once the scaling of the contact radius with particle radius or Young's modulus was determined, the work of adhesion was calculated using either Equation (8) or (11). This enabled the predictions of the theories to be checked for reasonableness and self consistency. However, errors in the estimated values of the Young's moduli, yield stresses, and hardnesses, for the present coatings, would make such estimates too crude to be of much value other than to say that they are within the order of magnitude of the previously-reported values.

The substrates used in previous studies were thick compared with the size of the particles. Presently, the particles are comparable with, or greater in size than, the 10 μm thick coating and the depth of penetration of the particles into some of the substrates is relatively large. These conditions raise two questions. Firstly, does the underlying substrate affect the size of the contact radius or the depth of penetration for any of these coatings? Secondly, it is conceivable that the plasticizer and the styrene butylacrylate form phase-separated regions, with predominantly the plasticizer in contact with the particles. This could result in apparent contact radii and depths of penetration which are determined by a layer plasticizer rather than by the bulk properties of the coating.

In order to address both of these issues, 25 and 50 μm thick coatings of the styrene butylacrylate with 20% plasticizer were made in a manner similar to that of the 10 μm thick coating, with the coating thickness controlled using a doctor blade.* As the solutions of coating material were the same in all instances, with the only change being the size of the spacing of the doctor blade, if phase separation were to occur, the thicker coating layers would be expected to have thicker layers of plasticizer. This would result in a greater apparent penetration depth of the particle. In addition, if the contact radius and penetration depth were, in some fashion, being restricted by the underlying Estar^{TM} support, variations in the coating thickness should result in variations in the size of the contact. As discussed earlier in this paper, SEM micrographs of cross sections of the coatings verified their thicknesses and failed to show any indication of phase-separated regions.

Figure 7 shows nominal 4 μm radius glass particles on the 25 μm (Figure 7a) and 50 μm (Figure 7b) thick coatings. Figure 8a and 8b show nominal 11 μm radius glass particles on the same coatings, respectively. No differences, within experimental error, were observed for either the contact radii or depth of penetration of the

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* A doctor blade is a blade with a predetermined, fixed opening and is used to control the thickness of fluid layer spread on a substrate. It is commonly used in the graphic arts industry.

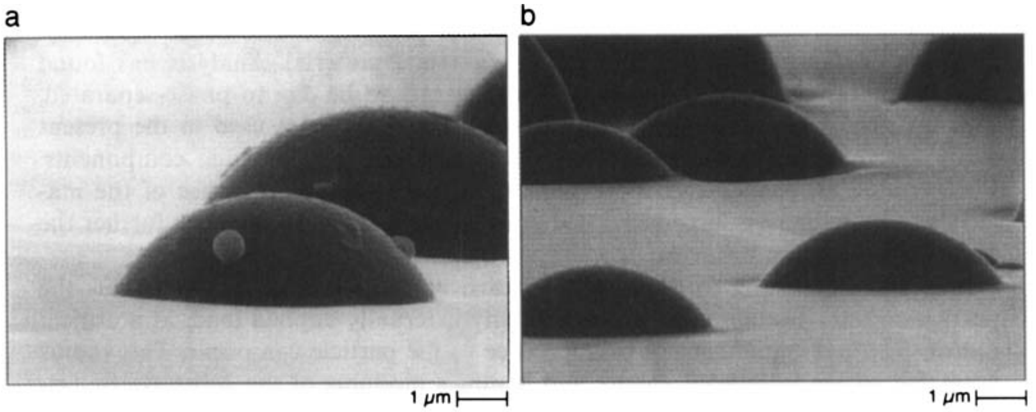

FIGURE 7 SEM micrographs of nominal 4 μm radius particles on 25 μm (7a) and 50 μm (7b) thick styrene butylacrylate coatings containing 20% plasticizer.

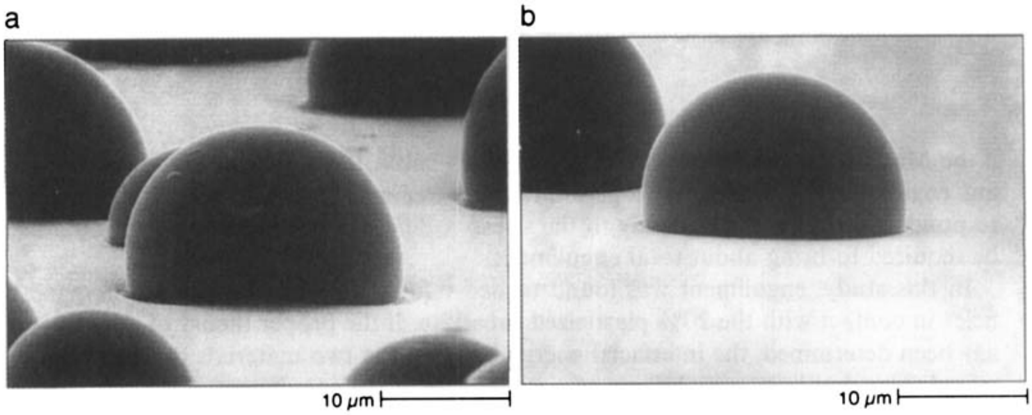

FIGURE 8 SEM micrographs of nominal 11 μm radius particles on 25 μm (7a) and 50 μm (8a) thick styrene butylacrylate coatings containing 20% plasticizer.

particles into the substrates. These results argue that, even for the 10 μm thick coating, the underlying substrate played a minimal role in determining the size of the surface-force-induced deformations. In addition, there does not appear to be any effect due to phase separation.

An interesting feature is noticed, however, around many of the particles. As expected, menisci are visible. These are consistent with the occurrence of tensile interactions, such as those discussed in the JKR model.[6] However, adjacent to many of these menisci are depressions. These suggest that the material flowing up the sides of the particles to form the menisci may be viscoelastically drawn from the regions surrounding the particles. These menisci differ from those reported earlier for a variety of particles on an alternating block polyester-polydimethylsiloxane copolymer.[20-22] Although the menisci in both instances appear to arise from viscoelastic flow of the substrate material, in the latter case the material appears to flow smoothly up multiple layers of particles and to cause significant amounts of interparticle bridging by the substrate material. Analysis has found that, in the latter case, the observed creep appears to be due to phase-separated, siloxane-rich polyester material.[23] In contrast, the substrates used in the present study are homogeneous and lack the low surface energy siloxane components. Further studies, particularly those relating to the temporal response of the materials to the adhesion-force-generated stresses, are needed to elucidate further the observed creep-type behavior.

It is also interesting to examine the case where the contact radius equals the particle radius. Assuming the absence of any externally-applied load, at a critical radius, R_c, total engulfment or submergence of the particle can occur. This radius is related to the interfacial energy and Young's modulus of the substrate by (assuming $\nu \sim 1/2$)

$$R_c = 7(\gamma_{12}/E) \tag{12}$$

if the deformations are described by the JKR model and by

$$R_c \approx 2\gamma_{12}/3Y \tag{13}$$

if the Maugis-Pollock theory of adhesion is applicable. If viscoelastic creep is occurring, engulfment can occur over a period of time. Depending on whether the substrate responds elastically or plastically to the stresses, different interfacial energies would be required to bring about total engulfment.

In this study, engulfment was found to occur for the nominal 4 μm radius particles in contact with the 20% plasticized substrate. If the proper theory of adhesion has been determined, the interfacial energy between the two materials can be determined. This, however, may be non-trivial. Because of the engulfment of the particles by the substrate, it is not possible to determine explicitly the mechanical nature of the deformation. However, it was found in this study that the adhesional contact between the substrate containing 10% plasticizer and the particles appeared to behave in a manner consistent with the predictions of the JKR model, whereas the contact between the particles and the substrate containing 5% plasticizer appeared describable by the Maugis-Pollock theory. This is reasonable because, at 10% plasticizer concentration, the substrate is beginning to behave like an elastomer. This suggests that the engulfment of the particles by the present substrate may be describable by the JKR theory. However, judging from the occurrence of depressions or "feet" adjacent to the contact regions, the engulfment looks to be more viscoelastic, arguing that the Maugis-Pollock model may be more appropriate. Recent experimental studies of the contact radius as a function of particle radius for highly compliant substrates[19] suggest that neither model is correct and that further theoretical developments are needed, but that the JKR model comes closer to predicting the contact radius for such systems of particles and substrates. Accordingly, the interfacial energy was calculated using the JKR model. Assuming that $R_c = 4$ μm and that $E = 10^5$Pa, the interfacial energy, γ_{12}, was estimated to equal 0.029 J/m^2. This is a very reasonable value for this particle-substrate system.

CONCLUSIONS

Micrometer-size glass particles were deposited onto plasticized styrene butylacrylate coatings and the resulting surface-force-generated contact radii were measured. For coatings which were in the glassy phase, the contact radius was found to vary as the square root of the particle radius. This result, which is consistent with the predictions of the Maugis-Pollock theory of adhesion[13] suggests that, in this instance, the substrate deformed plastically. This is in contrast to the 2/3 power law dependence observed when the coating material was plasticized sufficiently so as to be in the transition or rubbery phase. This response is consistent with the predictions of the JKR model of adhesion,[6] which assumes elastic response.

Menisci, suggestive of tensile interactions, were also observed. In addition, the substrate material causing the menisci was observed to form craters around many of the particles. This suggests that the material may be flowing viscoelastically in response to the surface-force-generated stresses.

Engulfment of the nominal 4 μm radius glass particles by the styrene butylacrylate substrate containing 20% plasticizer was observed. Assuming that this system is describable by the JKR theory of adhesion, the interfacial energy between the particle and the substrate was calculated to equal 0.029 J/m^2.

Finally, the techniques and observations reported herein can be used to generate much information about the fundamental adhesive properties of polymeric coatings.

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References

1. R. S. Bradley, *Philos. Mag.* **13**, 853 (1932).
2. R. S. Bradley, *Trans. Faraday Soc.* **32**, 1088 (1936).
3. B. V. Derjaguin, *Kolloid Z.* **69**, 155 (1934).
4. W. W. Merrill, A. V. Pocius, B. V. Thakker, and M. Tirrell, *Langmuir* **7**, 1975 (1991).
5. H. Krupp, *Advan. Colloid Interface Sci.* **1**, 111 (1967).
6. K. L. Johnson, K. Kendall and A. D. Roberts, *Proc. R. Soc. London, Ser. A* **324**, 301 (1971).
7. L. P. DeMejo, D. S. Rimai and R. C. Bowen, in *Particles on Surfaces 2: Detection, Adhesion, and Removal*, K. L. Mittal, Ed. (Plenum, New York, 1989), p. 49–58.
8. L. P. DeMejo, D. S. Rimai and R. C. Bowen, in *J. Adhesion Sci. Technol.* **5**, 959 (1991).
9. D. M. Schaefer, M. Carpenter, B. Gady, R. Reifenberger, L. P. DeMejo, and D. S. Rimai, submitted to *J. Adhesion Sci. Technol.*
10. D. S. Rimai, L. P. DeMejo, and R. C. Bowen, *J. Appl. Phys.* **68**, 6234 (1990).
11. D. S. Rimai, R. S. Moore, R. C. Bowen, V. K. Smith, and P. E. Woodgate, *J. Mater. Res.* **8**, 662 (1993).
12. D. W. van Krevelen, *Physics of Polymers* (Elsevier, Amsterdam, 1976). See also, I. M. Ward, *Mechanical Properties of Solid Polymers* (Wiley, New York, 1990) and J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980).
13. D. Maugis and H. M. Pollock, *Acta Metall.* **32**, 1323 (1984).
14. L. N. Rogers and J. Reed, *J. Phys. D* **17**, 677 (1984).
15. J. Reed, in *Particles on Surfaces 2: Detection, Adhesion, and Removal*, K. L. Mittal, Ed. (Plenum, New York, 1989), p. 3–17.
16. S. Wall, W. John, and S. L. Goren, in *Particles on Surfaces 2: Detection, Adhesion, and Removal*, K. L Mittal, Ed. (Plenum, New York, 1989), p. 19–34.

17. D. S. Rimai, L. P. DeMejo, W. Vreeland, R. C. Bowen, S. R. Gaboury, and M. W. Urban, *J. Appl. Phys.* **17**, 2253 (1992).
18. D. S. Rimai, L. P. DeMejo, and R. C. Bowen, *J. Appl. Phys.* **66**, 3574 (1989).
19. D. S. Rimai, L. P. DeMejo, and R. C. Bowen, to be published.
20. L. P. DeMejo, D. S. Rimai, J. Chen, and R. C. Bowen, *J. Adhesion* **39**, 61 (1992).
21. L. P. DeMejo, D. S. Rimai, J. Chen, and R. C. Bowen, to be published.
22. J. K. Vrtis, C. D. Athanasiou, R. J. Farris, L. P. DeMejo, D. S. Rimai, submitted to *J. Adhesion Sci. Technol.*
23. L. P. DeMejo, D. S. Rimai, and R. C. Bowen, J. Chen, and T. H. Mourey, unpublished results.