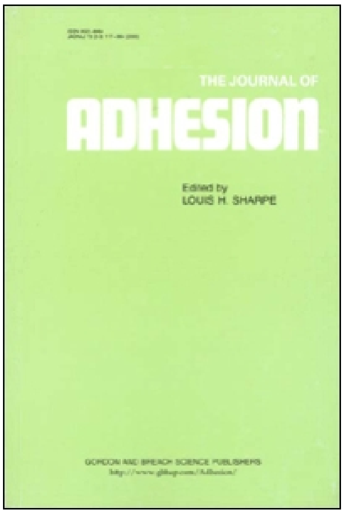

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Adhesion Induced Flow of a Soft Polyester-Polydimethylsiloxane Copolymer Substrate Over Micrometer and Submicrometer Size Spherical Particles: Observations of Anomalously Large Menisci, Interparticle Bridging and Particle Encapsulation

L. P. Demejo[a]; D. S. Rimai[a]; J. Chen[a]; R. C. Bowen[b]
[a] Research and Technology Development, Eastman Kodak Company, Rochester, NY, U.S.A. [b] Analytical Technology Division, Eastman Kodak Company, Rochester, NY, U.S.A.

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Adhesion Induced Flow of a Soft Polyester-Polydimethylsiloxane Copolymer Substrate Over Micrometer and Submicrometer Size Spherical Particles: Observations of Anomalously Large Menisci, Interparticle Bridging and Particle Encapsulation

L. P. DEMEJO, D. S. RIMAI,* J. CHEN

Research and Technology Development, Eastman Kodak Company, Rochester, NY 14650, U.S.A.

R. C. BOWEN

Analytical Technology Division, Eastman Kodak Company, Rochester, NY 14650-2011, U.S.A.

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Observations made with a scanning electron microscope (SEM) provided direct evidence for a soft polyester-polydimethylsiloxane block copolymer substrate undergoing extensive surface-force-induced plastic deformation upon contact with micrometer or submicrometer size spherical particles. Anomalously large menisci were detected at the particle/substrate interfaces. Moreover, the substrate material appeared to bridge or encapsulate the particles. The heights of the contact menisci between the 2.2 micrometer radius polystyrene beads and the substrate were found to be approximately 0.4 micrometers; those between 3.6 micrometer radius glass spheres and the substrate were approximately 0.5 micrometers. The heights of the observed menisci were found to be large compared with the values calculated using Tabor's analysis (D. Tabor, *J. Colloid Interface Sci.* **58,** 2 (1977)) based on the elastic model proposed by Johnson, Kendall and Roberts (K. L. Johnson, K. Kendall, and A. D. Roberts, *Proc. R. Soc. London* **A. 324,** 301 (1971)). These results suggest that the surface-force-induced tensile stresses may have exceeded the elastic limit of the substrate or that the surface material has an unexpectedly low surface modulus.

KEY WORDS Polyester-polydimethylsiloxane; block copolymer substrate; alternating block copolymer; polystyrene beads; glass microspheres; polyvinylidene fluoride particles; adhesion-induced flow; surface-force-induced deformations; tensile stresses; menisci; interparticle bridging; elastic limit; surface modulus.

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*Corresponding author.

INTRODUCTION

Ever since Derjaguin[1] and Bradley[2,3] first described deformations of materials due to forces of adhesion, many investigators have studied these effects, both theoretically and experimentally. Krupp[4] was the first to postulate that the adhesive forces between a particle and a substrate could be sufficiently high to cause plastic flow. A few years later, Johnson, Kendall and Roberts[5] published the well-known JKR theory, which proposed that the size of the contact area is determined by both elastic tensile deformations occurring at the edge of the contact zone and elastic compressive forces operating in the middle. This model assumed no attraction beyond the contact zone. The contact radius was calculated as a function of particle radius and the Young's modulus of the two materials using thermodynamic arguments. Israelachvili and Tabor[6] made direct measurements of the surface forces between cylindrical sheets of mica arranged with their axes normal to each other (to simulate the geometry of a sphere on a flat surface) using multiple beam interferometry. Derjaguin, Muller and Toporov (DMT)[7] recognized the important contribution of tensile forces to the size of the contact area in a microscopic theory of adhesion which generalized the original Hertzian contact model, proposed by Derjaguin, to include tensile interactions. Their model assumed that the force of adhesion originated from van der Waals interactions and, in contrast to the JKR model, a significant contribution to the force of attraction came from outside of the contact radius. Two years later, Tabor[8] compared the JKR and DMT theoretical treatments of the interaction between an elastic sphere and a hard flat surface. In addition, Tabor, assuming the validity of the JKR model, calculated the height of the meniscus, h, outside the contact region for a hard sphere interacting with three types of materials: a soft rubber ($E = 10^6$ N/m^2), a thermoplastic ($E = 10^9$ N/m^2) and a hard solid ($E = 10^{11}$ N/m^2). According to Tabor, the height of the meniscus around the contact zone, h, is given by the sum of the Hertzian gap, h_c, plus the JKR tensile contribution, h_t, according to the following equations

$$h_c = \frac{8\sqrt{2}}{3\pi}\frac{a_0^2}{R}\left[\frac{r}{a} - 1\right]^{3/2} \tag{1}$$

and

$$h_t = \frac{4}{3}\frac{a_0^2}{R}\left(1 - 2\pi \sin^{-1} a/r\right) \tag{2}$$

and

$$h = h_c + h_t \approx \left[\frac{R\left(\frac{w_A}{2}\right)^2}{E^2}\right]^{1/3} \tag{3}$$

where r is an arbitrary distance from the center of the contact zone, R is the particle radius, a is the contact radius, a_0 is the contact radius under zero load, E is the

Young's modulus of the more compliant material and w_A is the work of adhesion. Figure 10 of Ref. [8] illustrates the relevant coordinates in Tabor's contact-mechanics analysis.

Tabor also showed that the contact radius predicted by the DMT model was approximately half of that predicted by the JKR theory. Tabor,[9] Derjaguin *et al.*,[10] and Muller *et al.*,[11] elaborated further on the relevance of the JKR and DMT approaches and showed that, depending on whether or not attractive forces existed outside the contact zone, the JKR model described lower surface energy and more compliant materials. The DMT model, on the other hand, described higher surface energy, more rigid materials. In view of the physical properties of the substrate used in this study, the JKR model was used to analyze the observed phenomena. Finally, Maugis and coworkers[12-15] generalized the JKR model to include the possibility of plastic deformation.

Experimental studies of adhesion-induced deformations of relatively large particles in contact with different substrates have been reported by Johnson *et al.*,[5] and Chaudri and Yoffe.[16] Similar investigations of small particles on substrates performed with nanoindentors have also been published.[15,17-22] More recently, direct observations of adhesion-induced deformations were made using scanning electron microscopy (SEM).[23-31] For glass and polystyrene particles having radii less than 5 micrometers on a polyurethane substrate ($E = 5 \times 10^6$ N/m^2), the measured power law dependence of the contact radius, a, on the particle radius, R, was larger than that predicted by the JKR and DMT linear elastic theories. Furthermore, sizeable menisci were observed suggesting that significant tensile interactions also occur.

To investigate surface force deformations of materials further and, in particular, the effect of tensile forces on substrate deformations, it was desirable to examine the contact of particles on a substrate having a Young's modulus between that of typical elastomers and that of a typical thermoplastic. For that reason, an alternating polyester-polydimethylsiloxane block copolymer, with a relatively low Young's modulus of 9.2×10^6 N/m^2, was prepared in our laboratories and examined as a soft substrate on which particles exhibiting a range of sizes, moduli and surface energies were deposited.

EXPERIMENTAL PROCEDURE

Glass, polystyrene and polyvinylidene fluoride (PVF_2) particles were gently sprinkled onto the polyester-polydimethylsiloxane substrate from a height of approximately 1 cm. The terminal velocity of particles in air deposited in this manner was sufficiently low that it would not account for the observed deformations.[32-34] The 3.6 micrometer glass spheres were obtained from Duke Scientific Corporation. Typical values for the Young's modulus of glass silicates[35] are approximately 6×10^{10} N/m^2. The polystyrene beads, approximately 2.2 micrometers in radius, were prepared using the swollen latex Ugelstad technique,[36] as modified by Hoskyns.[37] The Young's modulus of polystyrene[35] is reported to be 3×10^9 N/m^2. The PVF_2 particles (Kynar 301F™, manufactured by Pennwalt Corporation) had an average radius of approximately 0.15 micrometers and a Young's modulus[35] of approximately 1×10^9 N/m^2. The polyester-polydimethylsiloxane substrate had a Young's modulus of approximately 9.2×10^6 N/m^2 (as determined using an Instron tensile tester). Therefore, the moduli of all the particles selected were at least two orders of magnitude larger than that of the substrate and any observed adhesion-induced deformations would be, presumably, due to the compliance of the substrate. Moreover, the particles used in this study have all been used previously.[23-31]

The substrate selected for this investigation was a polyester-polydimethylsiloxane block copolymer that contained exactly alternating blocks of polyester and polydimethylsiloxane (PDMS). This copolymer differed from a polyester-polydimethylsiloxane block copolymer substrate used in our previous studies[25-27] (referred to as PSBC) which was a random copolymer of a polyester with polydimethylsiloxane blocks of uniform block length. The PSBC substrate had a Young's modulus of 5.7×10^8 N/m^2 (measured in our laboratory) which was almost two orders of magnitude higher than the Young's modulus of the copolymer substrate used in this study.

A size exclusion chromatogram of the block copolymer is shown in Figure 1. This copolymer exhibits a molecular weight distribution peaking at a polystyrene equivalent molecular weight (PEMW) of approximately 8×10^4 g/mole. Figure 1 also reveals the presence of a small fraction of material exhibiting a low molecular weight around a PEMW of 10^3 g/mole. To analyze for its homogeneity, the block

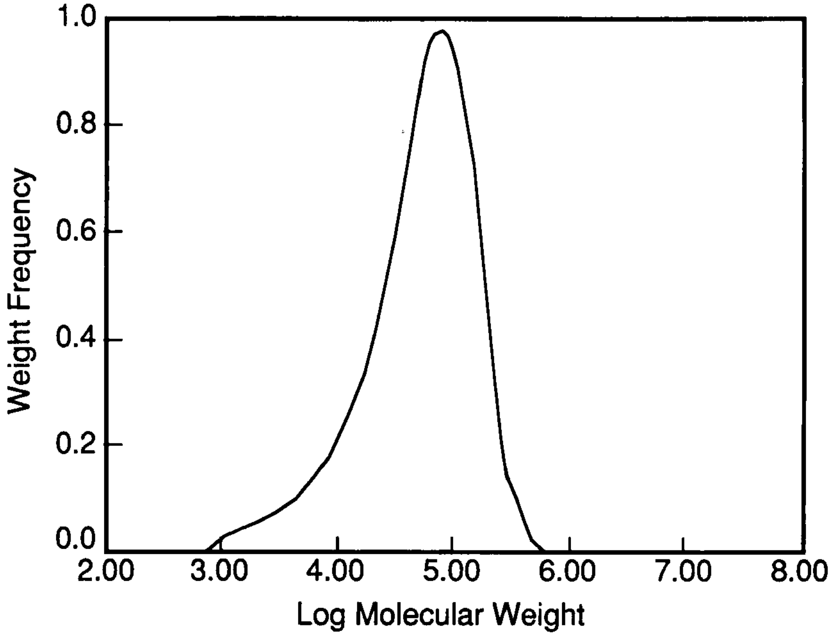


FIGURE 1 The molecular weight distribution of the polyester-polydimethylsiloxane alternating block copolymer substrate used in this study displayed as a polystyrene equivalent molecular weight distribution peaking at approximately 8×10^4 g/mole.

copolymer was first dissolved in dichloromethane. Next, heptane (a non-solvent for the polyester and a better solvent for the PDMS than dichloromethane) was added to the solution.[38] No phase separation was observed indicating the absence of any PDMS-rich cyclic or polymer. Furthermore, a solution of the copolymer in tetrahydrofuran exhibited a neutral pH and less than 0.002 meq/g amine was found by titration with perchloric acid. This indicated that essentially no amine terminated PDMS precursor existed in the block copolymer. On the other hand, the dimethylamine-terminated PDMS precursor was analyzed to exhibit 0.3 meq/g of amine endgroups which corresponded to an approximate number average molecular weight of 6670 g/mole.

The block copolymer was dissolved in methylene chloride at a concentration of 14.5 weight %. This solution was then poured into a circular Teflon™ mold such that after the solvent evaporated, a 5 mil thick film was cast against the Teflon™ surface. For the SEM studies, the particles were deposited on the smoother (air/polymer interface) side.

For one set of experiments the polyester-polydimethylsiloxane substrate was chromium coated prior to the deposition of the particles. A small chromium chunk was placed in a tungsten basket inside a Denton DV-502 High Vacuum evaporator. The substrate to be coated was mounted on a stage and rotated under $<10^{-6}$ Torr vacuum, while being gently heated, until evaporation of the chromium occurred. This procedure was followed in order to achieve a coating with a uniform thickness (approximately 500–1000 Å). However, the actual coating produced appeared discontinous (i.e., it exhibited numerous cracks).

The particle/substrate interactions were observed using the secondary emission from an SEM. Typically, the samples were mounted on a cold stage and coated with an electrically conductive 10 nm thick 60/40 gold/palladium coating by sputtering in an argon atmosphere for 60 s at 2.5 kV and 20 mA in a Polaron E5100 high resolution sputter coater. It was found that the temperature rise during sputtering was less than 20°C. The samples were mounted on cross-sectional stubs so they could be examined at high tilt angles (88° or, occasionally, 80° to the normal of the plane of the substrate) in a Philips 515 SEM, after allowing any residual stresses to relax for a period of approximately two weeks. The accelerating voltage and beam size were 30 kV and 10 nm, respectively. The range of magnifications selected were 1000× to 40,000×.

RESULTS

A typical SEM micrograph, showing 2.2 micrometer radius crosslinked polystyrene beads in contact with the polyester-polydimethylsiloxane copolymer substrate is shown in Figure 2. A magnification scale is shown below the micrograph. As can be seen, large contact areas and large menisci are observed between the particles and the substrate, indicating significant tensile deformations. Moreover, Figure 2 clearly shows the bridging of particles by an undefined material either on the substrate or on the particles.

To determine whether the unknown adhesive material originated from the parti-

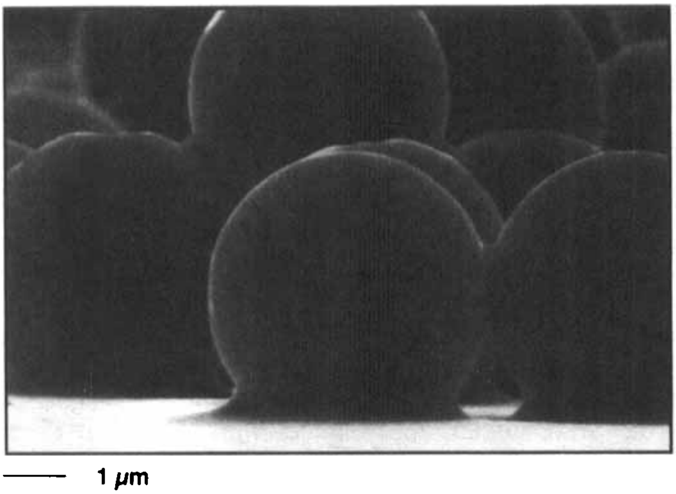


FIGURE 2 An SEM micrograph, showing the 2.2 micrometer radius polystyrene beads in contact with the polyester-polydimethylsiloxane copolymer substrate. Large contact areas, large menisci and interparticle bridging are observed suggesting significant tensile deformation and flow of the substrate material. A magnification scale is shown underneath the micrograph.

cles or from the substrate, 3.6 micrometer radius glass particles were gently sprinkled on the same polyester-polydimethylsiloxane copolymer substrate as well as on a polyurethane substrate used in a previous investigation.[29,31] Similarly large menisci were observed in the case of the glass particles on the polyester-polydimethylsiloxane copolymer substrate (Figure 3) as for the polystyrene particles on the same substrate (Figure 2). In contrast, the same glass particles on a different polyurethane substrate were observed to be clumped but neither bridged by adhesive material nor forming large menisci at the particle/substrate interface (Figure 4). These observations lead to the conclusion that the "adhesive" material was coming from the surface of the polyester-polydimethylsiloxane substrate. Furthermore, no observable changes in the meniscus sizes and the extent of bridging were noted after samples of the polystyrene particles (Figure 5A) and glass particles (Figure 5B) deposited on the same copolymer substrate were degassed for one week at 10^{-6} Torr. All these experimental observations indicated actual flow of substrate material up the particles rather than evaporation of volatile material from the substrate followed by recondensation of the same material on the particles. Unless further degradation and fractionation of the copolymer had occurred during the preparation of the solvent cast film, the rigorous methods used to synthesize, isolate and purify this copolymer would have already removed any volatile cyclic oligomer species from the block copolymer substrate. The observation that even polystyrene particles on a three particle high stack were bridged by the "adhesive" material (Figure 5A) suggested that the flow of substrate material up the particles had occurred after particle deposition, as opposed to the particles picking up the "adhesive" after rolling over the substrate.

To try to prevent this unusual substrate flow phenomenon, chromium was evapo-

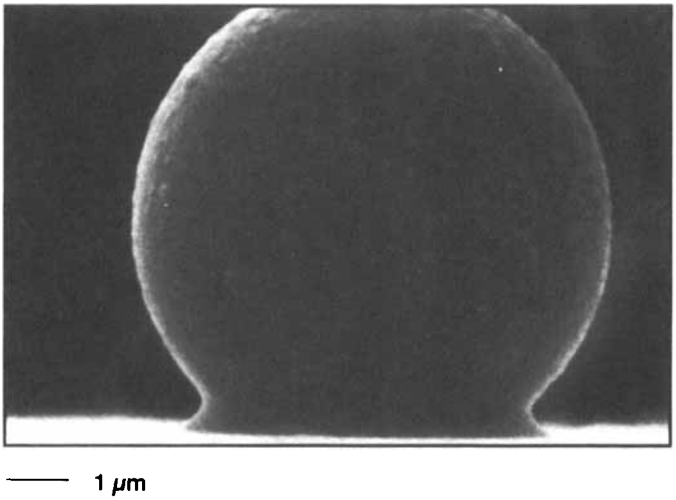


FIGURE 3 An SEM micrograph of a representative 3.6 micrometer radius glass microsphere on the polyester-polydimethylsiloxane copolymer substrate. Large contact menisci are observed indicating substantial tensile deformation. The appropriate magnification is indicated under the micrograph.

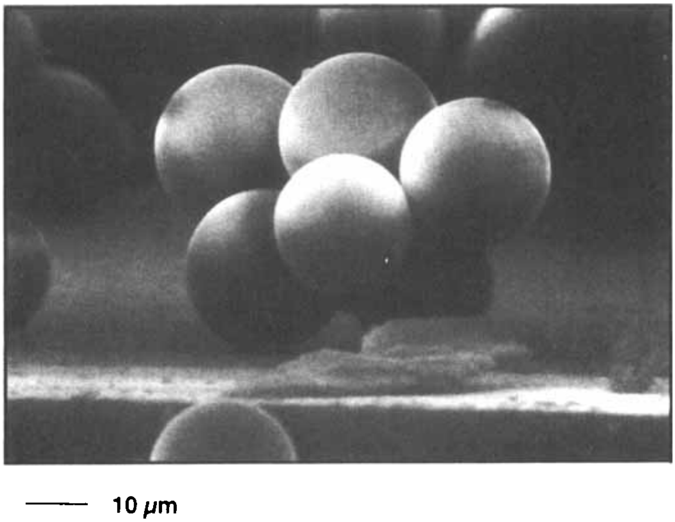


FIGURE 4 SEM micrograph of 10 micrometer radius glass microspheres contacting a polyurethane substrate. These microspheres are from the same batch as the 3.6 micrometer radius glass microsphere shown in Figure 3. No large menisci nor interparticle bridging were observed. This evidence eliminates the possibility that the adhesive material originated from a contaminant on the glass microspheres. A magnification scale is included with the micrograph.

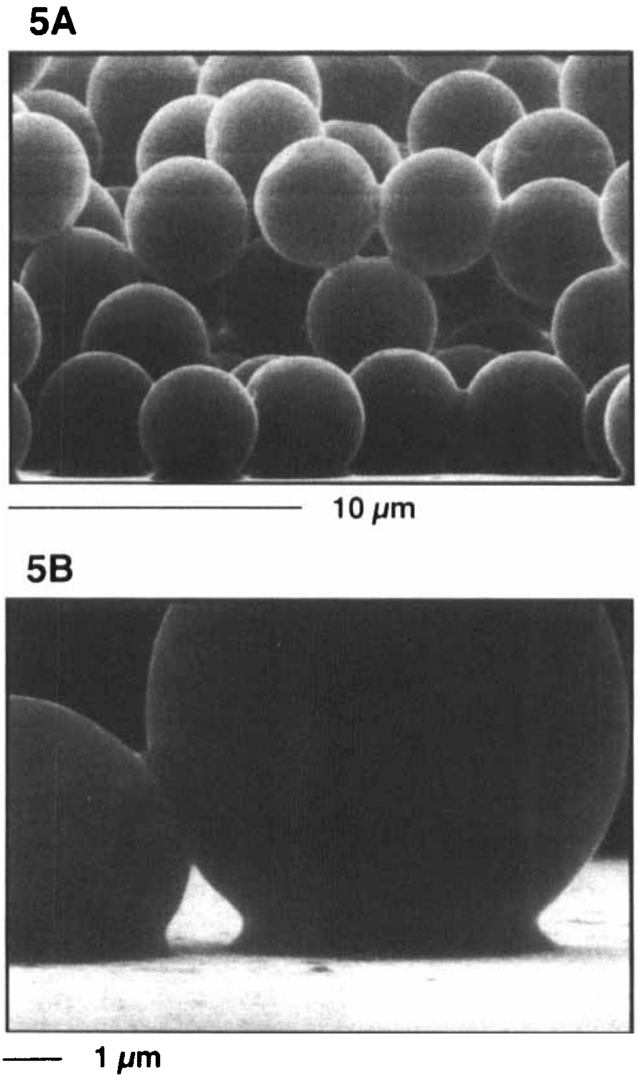
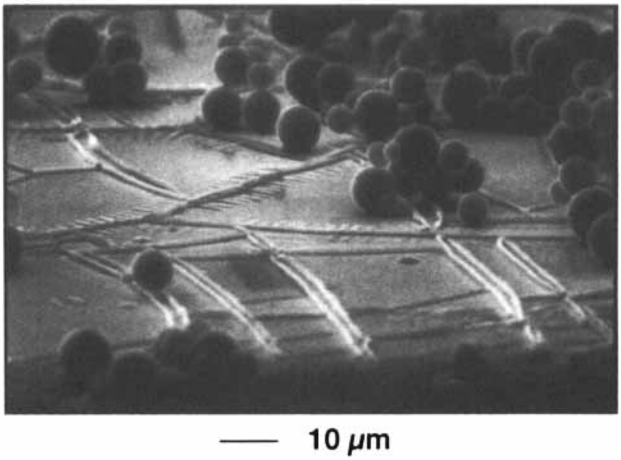


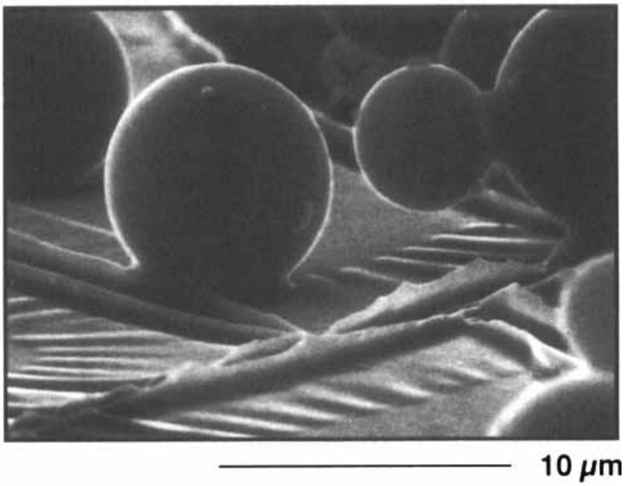
FIGURE 5 SEM micrographs of 2.2 micrometer radius polystyrene beads (5A) and 3.6 micrometer radius glass microspheres (5B) on the same polyester-polydimethylsiloxane copolymer substrate after each sample was outgassed for one week at 10^{-6} Torr inside the SEM chamber. The large contact menisci and interparticle bridging are still detected. Even polystyrene particles on a three particle high stack were bridged by "adhesive" material originating from the substrate (5A). Appropriate magnification scales are shown.

FIGURE 6 SEM micrographs of glass microspheres in contact with a chromium coated polyester-polydimethylsiloxane copolymer substrate. The chromium was evaporated on the substrate prior to the deposition of the particles. Nevertheless, the chromium coating exhibited cracks or ridges in it and could not prevent the formation of the large contact menisci and interparticle bridging. Figures 6A, 6B and 6C correspond to micrographs of the same field at increasing magnifications, respectively. The appropriate scales are also shown.

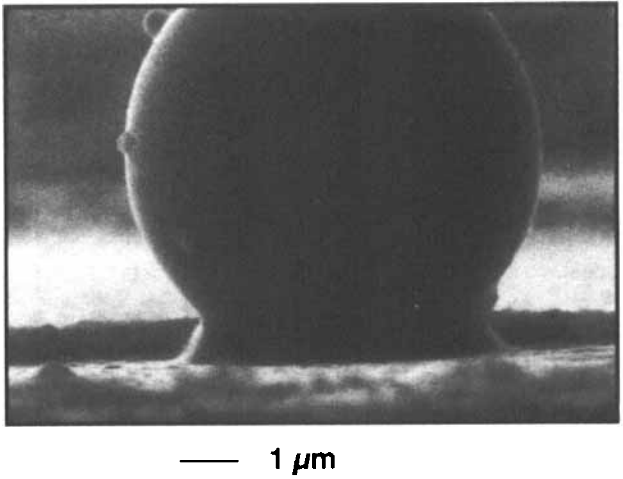
6A



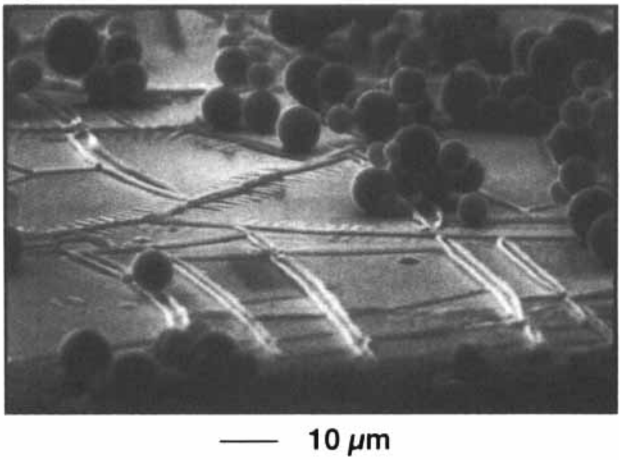
6B



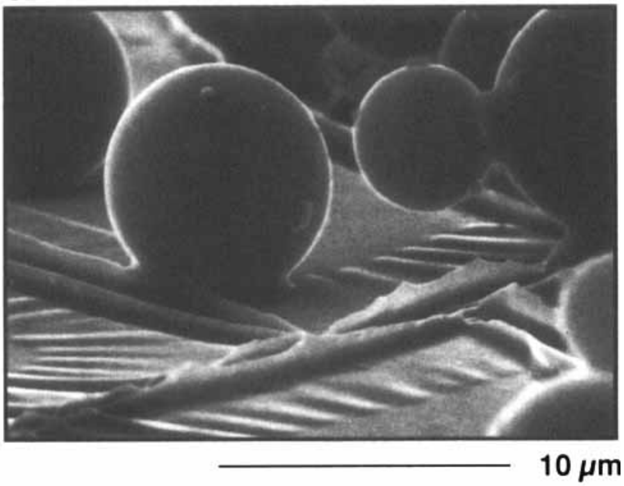
6C



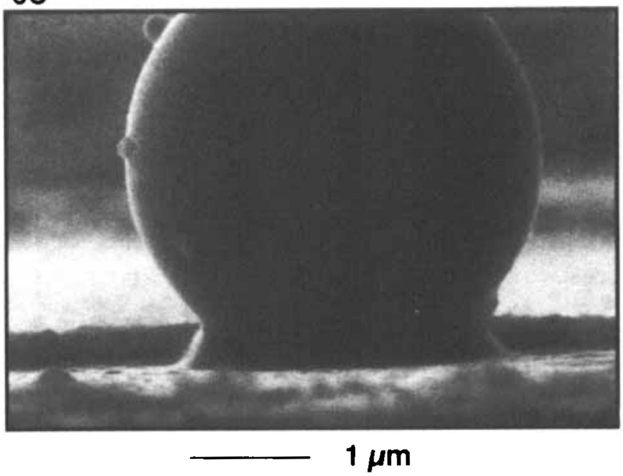
6A



6B



6C



rated onto a piece of the polyester-polydimethylsiloxane copolymer substrate prior to the deposition of the particles. However, micrographs of the glass particles on the chromium coated surface (Figures 6A–6C) indicated that the coating exhibited cracks or ridges in it and that similarly large menisci and particle bridging phenomena could be observed as in the previous cases. It appeared that the substrate material was able to "seep" through the cracks and once again flow up the particles either during or after the chromium evaporation process.

SEM micrographs of the PVF_2 particles, (Figures 7A–7C) show the individual particles or particle clumps to be completely encapsulated by the substrate material. Furthermore, Figure 7B shows particles that appear to sink deeper into the substrate. This may be due to the higher tensile stresses at the edge of the contact zone which draw the encapsulating "skin" from the center toward the edge, thus enhancing the compressive forces acting on the particles in the center of the contact zone. The additional contribution to the compressive stress would then cause the particles to sink deeper into the softer substrate.

As discussed previously in this paper, Tabor calculated the height of the meniscus, h, at the edge of the contact zone using the JKR model.[8] In his analysis, he made two assumptions. The first was that linear elasticity holds over the whole range of deformations. Tabor recognized that this assumption was not strictly valid for deformations occurring at the sharp edge of the contact zone. The second criterion was that the interfacial forces outside the contact region were negligible. Tabor admitted that this assumption was incorrect when the value for the meniscus height became less than or equal to the equilibrium separation distance $z_0 = 3$ Å. Therefore, even without a detailed contact-mechanics analysis, a strictly linear elastic solution for this case would still be expected to yield a larger contact area than predicted by Tabor's analysis.

One can measure the meniscus heights of the particle/substrate contacts for both the polystyrene beads and the glass microspheres and compare the measured heights with those calculated using Eq. (3) (Tabor's approximation based on the JKR theory).[8] The results are summarized in Table I. The works of adhesion that were used for the calculations were assumed to be 0.07 J/m^2 for the polystyrene beads and 0.17 J/m^2 for the glass microspheres, based on the contact area obtained for similar particles on polymeric substrates.[28,31]

The observed meniscus heights are approximately an order of magnitude larger than the calculated values for the 2.2 micrometer radius polystyrene beads and half an order of magnitude larger than the values calculated for the 3.6 micrometer radius glass microspheres. Since the calculations are based on a linear elastic model using assumptions that disregarded localized effects at the edge of the contact zone, this discrepancy between experiment and theory is not surprising..

FIGURE 7 SEM micrographs of 0.15 micrometer radius polyvinylidene fluoride beads contacting the polyester-polydimethylsiloxane copolymer substrate. These pictures, show the individual particles or particle clusters to be completely encapsulated by the substrate material. Figures 7A and 7B show individual particles that appear to sink even deeper into the substrate. The forces which drive these particles further into the substrate are believed to originate at the edge of the contact. Appropriate magnification scales are also indicated.

TABLE I

Mean particle radii and contact meniscus heights (measured and calculated using equation (3)) for polystyrene and glass particles on a polyester-polydimethylsiloxane block copolymer substrate. Also listed are the number of particles examined, the standard deviation of the observed dimensions and the statistical error in the particle radius, t_R, and contact meniscus height, t_C, as estimated using the Student's test at the 95% confidence level

					Contact meniscus height (μm)			
Type of particle	No. of particles	Particle radius (μm)	Std. dev. (μm)	t_R (μm)	Measured	Std. dev.	t_C	Calc. using Eq. (3)
Polystyrene	5	2.22	0.03	0.05	0.41	0.04	0.06	0.03
Glass	6	3.58	0.39	0.50	0.48	0.07	0.09	0.07

As previously discussed, the initial chemical characterization of the copolymer substrate did not identify free polydimethylsiloxane homopolymer. This analysis does not support the hypothesis of a pure silicone fluid on the surface of the substrate as the mobile phase responsible for the observed phenomena. If the surface layer on the substrate was a viscoelastic material rather than a fluid, then the observations suggest that the edge tensile stresses may have exceeded the elastic limit of this material. Alternatively or in addition, a surface layer exhibiting a lower modulus than that of the bulk material could also account for these observations. Recent chemical analysis of the solvent-cast substrate film has, in fact, revealed extractable high molecular weight and low molecular weight silicone-rich polyester fractions that may very well be concentrated at the surface of the substrate and exhibit fluid-like behavior.[39] An enriched surface layer in polymer blends has been previously observed and reported by Jones and Composto and coworkers.[40,41]

Gent[42] has recently proposed that there is a critical particle radius, R_c, below which severe swallowing or engulfment will occur. This radius is given by

$$R_c \approx 5-10\,(\gamma_{12}/E), \tag{4}$$

where γ_{12} is the interfacial energy and E is the Young's modulus of the substrate. This relationship follows from simple scaling considerations.

Using Gent's approach to predict R_c for the engulfment of the PVF_2 particles into the polyester-polydimethylsiloxane copolymer substrate, the interfacial energy, γ_{12}, can be calculated from the work of adhesion, w_A, and the surface energies of the interacting materials, γ_1 and γ_2, according to

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

Following the arguments of Pashley and Tabor for totally inelastic deformations[19] and assuming no externally applied load, the work of adhesion, w_A, can be derived from the contact radius, a, the hardness of the substrate, H, and the particle radius, R according to

$$w_A=H\,a^2/2R, \tag{6}$$

where the hardness is assumed to be approximately 1% of the Young's modulus of the substrate and $a \approx R$, as observed from Figures 7A and 7B. For $R_{PVF_2} = 0.15$ micrometers and $H_{substrate} = 10^5$ N/m^2, $w_A = 0.007$ J/m^2. Inserting this value for the work of adhesion as well as the surface energies of the PVF_2 particles and the substrate (namely 0.025 J/m^2 and 0.030 J/m^2, respectively) into Eq. (5) yields an interfacial energy γ_{12} of 0.048 J/m^2. Substitution into Eq. (4) leads to the prediction that $R_c \approx 0.025$–0.05 micrometers. In other words, the PVF_2 particles would have to be at least two-thirds smaller in size before the particle radius would equal the critical radius with the polyester-polydimethylsiloxane copolymer substrate. For higher surface energy particles or for a higher surface energy substrate of lower modulus, this critical size would increase and vice versa.

CONCLUSIONS

Anomalously large menisci, interparticle bridging and particle encapsulation phenomena were observed between rigid micrometer size spherical particles and a polyester-polydimethylsiloxane alternating block copolymer substrate (Young's modulus $= 9.2 \times 10^6$ N/m^2). The observed menisci, which arise from surface-force-induced tensile interactions, are approximately an order of magnitude larger than expected from Tabor's analysis of adhesion-induced deformations based on the JKR theory. These results may be due to the substrate surface layer having an unexpectedly low modulus. Alternatively, the tensile stresses may have exceeded the elastic limit of the substrate surface layer.

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