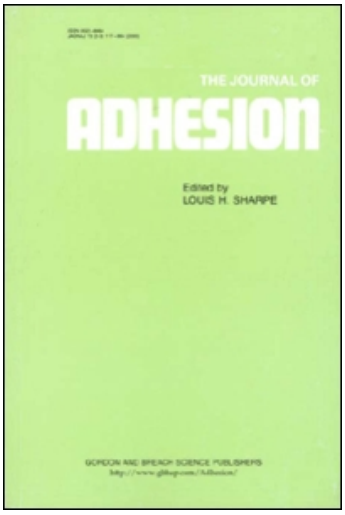

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Time Dependent Adhesion Induced Phenomena: The Flow of a Compliant Silicone-Polyester Copolymer Substrate Over Rigid Micrometer Size Gold and Polystyrene Particles

L. P. Demejo[a]; D. S. Rlmal[a]; J. H. Chen[a]; R. C. Bowen[b]

[a] Office Imaging Research and Technology Development, Eastman Kodak Company, Rochester, NY, U.S.A. [b] Analytical Technology Division, Eastman Kodak Company, Rochester, NY, U.S.A.

To cite this Article Demejo, L. P. , Rlmal, D. S. , Chen, J. H. and Bowen, R. C.(1995) 'Time Dependent Adhesion Induced Phenomena: The Flow of a Compliant Silicone-Polyester Copolymer Substrate Over Rigid Micrometer Size Gold and Polystyrene Particles', The Journal of Adhesion, 48: 1, 47 — 56

To link to this Article: DOI: 10.1080/00218469508028153

URL: http://dx.doi.org/10.1080/00218469508028153

J. Adhesion, 1995, Vol. 48, pp. 47–56
Reprints available directly from the publisher
Photocopying permitted by license only

Time Dependent Adhesion Induced Phenomena: The Flow of a Compliant Silicone-Polyester Copolymer Substrate Over Rigid Micrometer Size Gold and Polystyrene Particles

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

Office Imaging Research and Technology Development, Eastman Kodak Company, Rochester, NY 14653-6402, U.S.A.

and

R. C. BOWEN

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

(Received January 16, 1994; in final form May 12, 1994)

A polyester-polydimethylsiloxane block copolymer substrate (Young's modulus of approximately 9.2×10^6 N/m^2) was observed by SEM to gradually creep over higher modulus gold and polystyrene micrometer sized particles in contact with its surface. The particle/substrate and particle/particle interfaces were examined shortly after particle deposition and again at various intervals up to a month later. SEM micrographs clearly showed an increase in the size of the contact menisci with time (for periods up to approximately two weeks) at both sets of interfaces. After only one week the gold particles appeared to be completely encapsulated by the substrate. These time-dependent observations confirm the plastic deformation mechanism proposed previously to explain similar observations on micrometer- and submicrometer-sized glass, polystyrene, and poly-vinylidene fluoride beads contacting the same substrate (L. P. DeMejo, D. S. Rimai, J. Chen, and R. C. Bowen, *J. Adhesion* **39**, 61 (1992)).

KEY WORDS Polyester-polydimethylsiloxane block copolymer substrate; gold particles; polystyrene beads; adhesion induced deformations; interparticle bridging; elastic and plastic deformations; plastic flow; creep.

INTRODUCTION

Adhesion-induced deformation phenomena have been modelled theoretically and observed experimentally over the past 60 years.[1–36] These effects were first postulated independently by Derjaguin[1] and Bradley.[2,3] Later, Krupp postulated that surface-force-induced stresses could be large enough to exceed the elastic limit of at least one of the interacting materials.[4]

*Corresponding author.

The JKR model,[5] proposed by Johnson *et al.*, in 1971, assumes that tensile interactions, in addition to compressive stresses, contribute to the size of the contact radius. The model assumes that all interactions occur within the contact zone and result exclusively in elastic deformations. According to this theory, in the absence of any externally applied load, the relationship between the contact radius, a, and the particle radius, R, for a rigid particle in contact with a compliant substrate, is given by

$$a^3 = 0.75[6w_A\pi R^2]\frac{(1-\nu^2)}{E} \tag{1}$$

where w_A is the thermodynamic work of adhesion, E is the Young's modulus of the compliant material (assumed to be significantly smaller than the Young's modulus of the other material) and ν is the Poisson's ratio of the compliant material.

Derjaguin, Muller and Toporov[7] (DMT) subsequently proposed a model which included the contribution of tensile interactions. However, unlike the JKR model, they assumed a Hertzian shape for the contact zone. As a result, the interactions were equipartitioned inside and outside the contact zone. The contact radius calculated using the DMT model was later shown by Tabor[8] to equal approximately one-half the radius calculated using the JKR theory. Muller and coworkers[11] showed that the discrepancies between the two models arose from the different assumptions regarding the contact zone and that each model had its own region of validity. The JKR theory best describes interactions between high surface energy, compliant materials whereas the DMT theory is valid for low surface energy, rigid substances.

Maugis and Pollock[14] allowed for the occurrence of plastic deformations within the formalism of the JKR model. Their model predicts, in the absence of an applied load, that

$$a^2 = \frac{2w_A R}{3Y} \tag{2}$$

where Y is the yield strength of the more compliant material.

Recently, anomalously large contact menisci, interparticle bridging and particle encapsulation, due to the adhesion-induced flow of a soft polyester-polydimethylsiloxane copolymer substrate over micrometer and submicrometer size spherical particles, have been observed with a scanning electron microscope (SEM).[33] These observations were usually made at least one week after the particles were deposited on the substrate. The contact diameter and the height of the contact menisci were significantly larger than those predicted by small deformation linear elastic theories such as the JKR theory.[5,8] Owing to the size of the deformation, it was hypothesized that the substrate deformed plastically. Permanent substrate deformations (craters), resulting from the surface forces between the polyester-polydimethylsiloxane copolymer substrate and gold or tin particles, were observed after these particles were removed by amalgamation with mercury.[34] This observation further supports the plastic flow mechanism proposed to explain the original results.

Chaudhury[35] also reported, independently, the observation of adhesion-induced interfacial creep and adhesion hysteresis. He investigated the contact between a crosslinked polydimethylsiloxane (PDMS) semispherical lens and the same crosslinked PDMS surface or PDMS surfaces chemically functionalized by plasma treatment alone or by the adsorption of self-assembled organic monolayers.

If the deformations are indeed plastic in nature, characteristic times associated with yielding or creep should be observed. Accordingly, in this study, the time dependence of the contact radius was determined for gold and polystyrene particles in contact with the same polyester-polydimethylsiloxane substrate that has been previously investigated.[33,34]

EXPERIMENTAL PROCEDURE

The polyester-polydimethylsiloxane copolymer substrate, described in earlier investigations,[33,34] was cast out of a 14.5% solution in methylene chloride onto a Teflon® surface. Polystyrene and gold particles were then deposited on the smoother (air/polymer interface) side of the copolymer substrate from a height of approximately 1 cm, to avoid gravitational contributions to the observed deformations.[37-39] The properties and source of the 3.6 μm radius polystyrene particles have been described previously.[36] The gold particles (average particle radius of 1.0 μm) were obtained from ALFA Chemicals, Inc. and they exhibited a broad size distribution and a spheroidal shape. As indicated in Table I, the Young's moduli of the gold and polystyrene particles were at least two orders of magnitude larger than that of the substrate. Therefore, only the substrate material would be expected to deform.

The particle/particle and particle/substrate interfaces were examined at approximately 88° tilt angle with the SEM equipment described previously.[33] After the particles were deposited on the substrate, 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 argon atmosphere. In general, the sputtering was done immediately prior to viewing the samples. In some instances, when it was desirable to determine if the coating impeded material flow, sputtering was done shortly after the particles were deposited on the substrate. The short time/low temperature sputtering conditions (60 seconds at 2.5 kv and 20 mA) were found previously not to contribute significantly to the observed deformations. The accelerating voltage and beam size for the scans were 30 kv and 10 nm, respectively.

TABLE I
Particle and substrate characteristics

Materials	Average particle radius (μm)	Young's modulus[33,40] (N/m^2)
Polystyrene	3.6	3×10^9
Gold	1.3	8×10^{10}
Polyester-polydimethylsiloxane		9×10^6

RESULTS

Figures 1A and 1B show two different fields of gold particles contacting the copolymer substrate viewed approximately 15 minutes after the samples were prepared and coated with the conductive coating. The particle/substrate interfaces appeared generally flat. Small menisci were observed, in some cases, at the perimeter of the contact zones. In areas where particles contacted each other, there did not appear to be any evidence of substantial flow of substrate material to the particle/particle interfaces.

However, after storing the samples for two weeks and then viewing them again, dramatic differences were noted, as shown in Figures 1C and 1D. Again, as reported previously,[34] large menisci had formed at the perimeter of the particle/substrate interfaces. Moreover, the flow of the substrate material over the particles was so extensive that it bridged their interfaces, thereby encapsulating them and merging several particles into agglomerates.

A similar experiment was conducted with the polystyrene microbeads. The particles were deposited on the substrate, coated and then viewed about 15 minutes after deposition (Figure 2A), four days later (Figure 2B), two weeks later (Figure 2C), and after one month (Figure 2D). Small contact menisci were observed shortly after deposition. After four days, the contact menisci at both particle/substrate

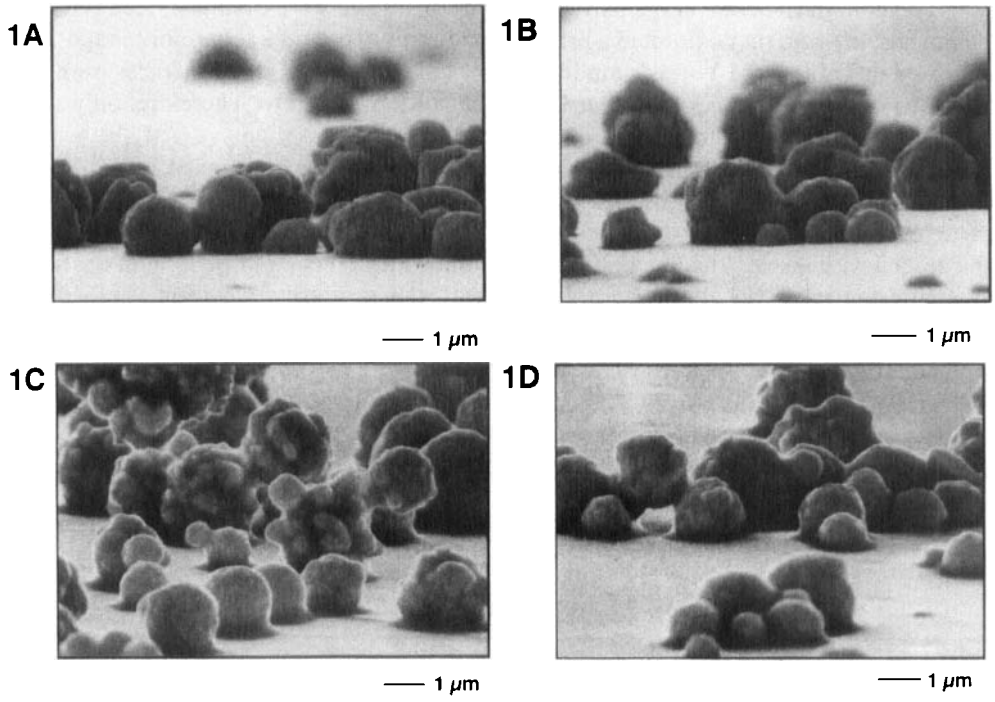

FIGURE 1 Scanning electron micrographs of 1.0 μm average radius gold particles on a polyester-polydimethylsiloxane copolymer substrate showing the time dependence of the plastic flow process (1A and 1B: 15 minutes after deposition; 1C and 1D: one week after deposition). Magnification scales are shown underneath each micrograph.

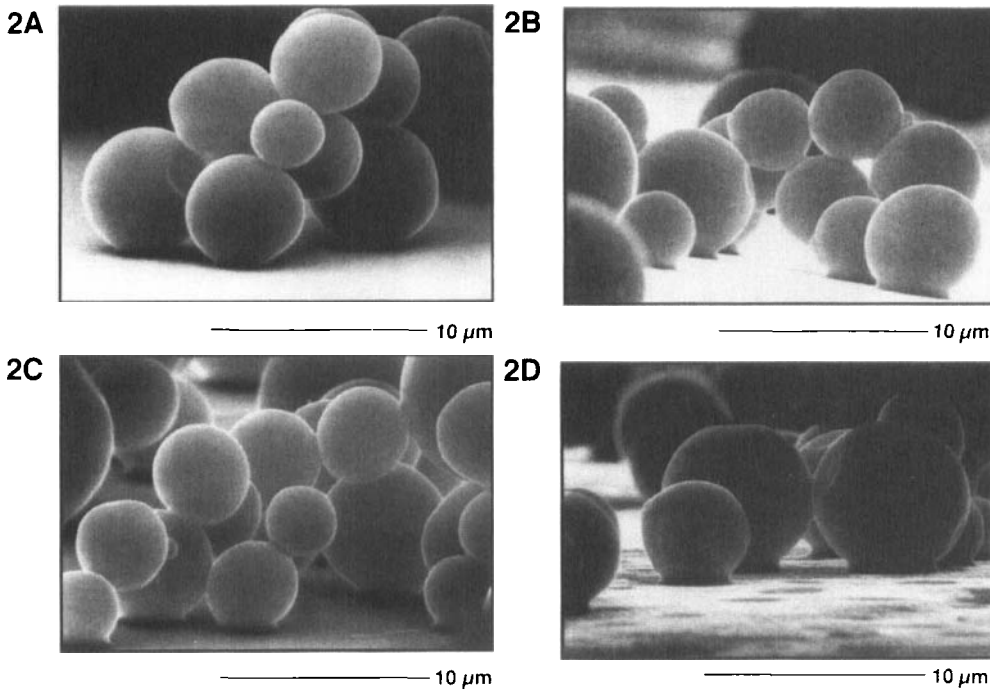

FIGURE 2 Scanning electron micrographs of 3.6 μm average radius polystyrene beads on a polyester-polydimethylsiloxane copolymer substrate showing the time dependence of the plastic flow process (2A: 15 minutes after deposition; 2B: 4 days after deposition; 2C: two weeks after deposition; and 2D: one month after deposition). The appropriate magnification is indicated underneath each micrograph.

and particle/particle interfaces were significantly more pronounced and increased only slightly between one and two weeks. No noticeable changes occurred after two weeks.

An interesting change in the substrate surface features was also detected. Initially, the surface appeared smooth or, at most, slightly rippled shortly after the particle deposition and the conductive coating evaporation steps (Figure 3A). However, after four days, distinct ridges or cracks had formed on the surface (Figure 3B). They were even more pronounced after two weeks (Figure 3C). These ridges or cracks could have developed in the gold/palladium coating if the coating was being constrained at each of the particle/substrate interfaces during the flow of the underlying sub-strate material.

To determine whether the conductive coating retarded the creep of the substrate material over the polystyrene beads, the following experiment was conducted. The beads were deposited onto the substrate. One portion of the specimen was sputter-coated immediately after the deposition, whereas the other was coated a week later. Figure 4A shows the results for the sample that was prepared and coated on the same day but viewed a week later. Figure 4B shows a micrograph of the sample representing the one week interval between particle deposition and sputter coating but viewed the same day it was coated. The contact menisci at the particle/particle and particle/substrate interfaces were distinctly less pronounced in the sample coated shortly

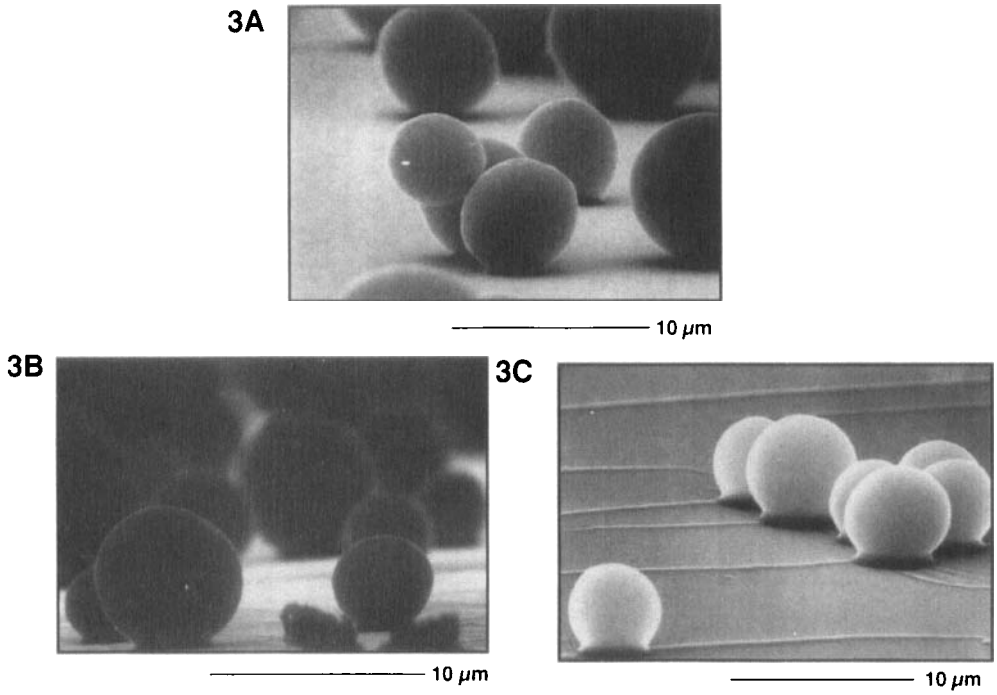

FIGURE 3 Scanning electron micrographs of 3.6 μm average radius polystyrene beads on a polyester-polydimethylsiloxane copolymer substrate 15 minutes after deposition (3A), 4 days after deposition (3B), and two weeks after deposition (3C). 3B and 3C show stress-induced surface features on the conductive coating due to flow of the underlying substrate. Magnification scales are included with each micrograph.

after the particle deposition and viewed a week later, confirming the hypothesis that the coating had retarded the flow of the underlying substrate. Figure 5B, when compared with Figure 5A, depicts a slight rippling of the coated surface viewed on the same day it was coated, as opposed to the sharper-ridges or cracks exhibited by the surface viewed

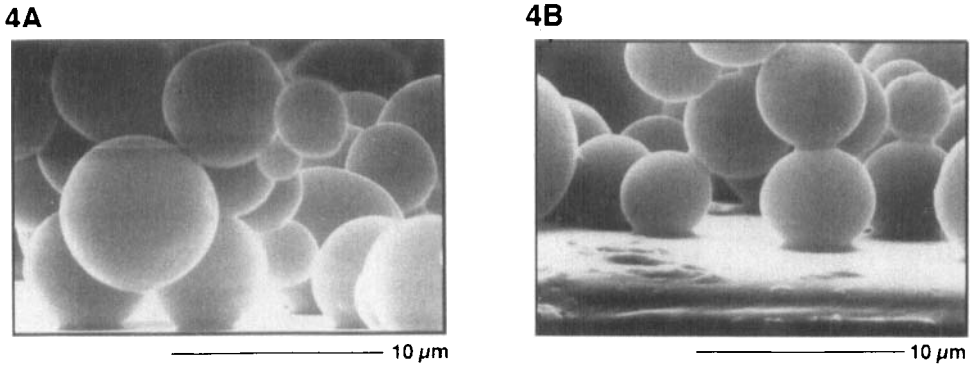

FIGURE 4 Scanning electron micrographs of 3.6 μm average radius polystyrene beads on a polyester-polydimethylsiloxane copolymer substrate showing retardation of the plastic flow process by the conductive coating. The sample coated one week before viewing (4A) shows smaller menisci than the sample coated and viewed one week after deposition (4B). Appropriate magnification scales are also indicated.

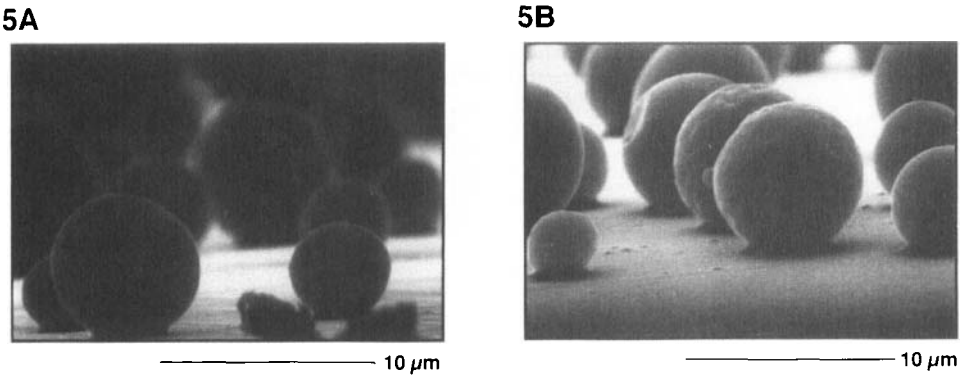

FIGURE 5 Scanning electron micrographs of 3.6 μm average radius polystyrene beads on a polyester-polydimethylsiloxane copolymer substrate showing differences in the surface features depending on when the sample was coated (5A: coated one week before viewing; and 5B: coated and viewed one week after deposition). Appropriate magnification scales are shown.

one week after the sample was coated. This lends further support to the stress-induced contraction mechanism proposed above.

In an earlier investigation of this same copolymer substrate, a number of experimental observations suggested that plastic deformation of the material on the surface of this copolymer substrate had occurred.[3,4] The most dramatic piece of evidence were the qualitative SEM micrographs showing the substrate material after it had crept up the particles. Furthermore, theoretical calculations were made of (a), the heights of the contact menisci between the polystyrene or glass microbeads and the substrate and (b), the critical radius for engulfment of polyvinylidene fluoride submicrometer particles into the substrate. These calculations, based on a small deformation linear elastic model,[5,8,41] grossly underestimated the experimentally-observed parameters.

By substituting appropriate values for the yield strength and for the average contact and particle radii into Equation (2), assuming typical literature values for the yield stress, Y, of approximately 0.003E, one can calculate the work of adhesion for the gold particles and for the polystyrene particles in contact with the polyester-polydimethylsiloxane substrate. The average contact and particle radii, determined from the micrographs for the gold particles, are approximately 1.0 μm each. Upon substituting these values and the estimated value for the yield strength of the substrate (2.7×10^4 N/m^2) into Equation (2), w_A was estimated to be approximately 0.041 J/m^2. This result is quite reasonable, especially in the highly likely event that the gold surface is coated with organic contaminants. The average contact and particle radii, determined from the micrographs for the polystyrene particles, were 2.4 and 3.6 μm, respectively. Substituting these radii into Equation (2) yields the value of 0.022 J/m^2 for the work of adhesion of the polystyrene particles in contact with the same substrate. Although this result may seem slightly lower than expected, in general, the interfacial energy between two solids is not known. Moreover, the strong dependence of w_A on R can introduce significant errors in the calculations.

Tabor[8] showed that the height of the contact meniscus, h, according to the JKR model,[5] is approximately related to the particle radius, work of adhesion and Young's

TABLE II
Contact meniscus heights on the polyester-polydimethylsiloxane substrate

Type of particle	Average particle radius (μm)	Average contact radius (μm)	Contact meniscus height (μm)		
			Measured	Calculated for elastic flow[5,8]	Calculated for plastic flow[8,14]
Polystyrene	3.6	2.4	0.4	0.08	0.4
Gold	1.0	1.0	0.4	0.02	0.4

modulus of the more compliant material (in this case, the substrate) by

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

This result is only valid for an elastically responding system. The value of h for the case of plastic flow can be estimated by substituting the hardness (which is approximately three times the yield strength[14]) for the Young's modulus in Equation (3). The estimates for the height of the contact menisci, assuming elastic deformation or plastic deformation, compared with the measured values obtained directly from the micrographs, are summarized in Table II. These measured values are in reasonable agreement with meniscus heights measured previously for similar size polystyrene, glass and gold particles on the same substrate.[33,34] Furthermore, they are in good agreement with the estimates of h assuming plastic flow. On the other hand, the elastic predictions significantly underestimate the measured meniscus heights.

More detailed analytical information concerning the subsrate's chemical heterogeneity, obtained recently, suggests that a silicone polyester copolymer is the mobile phase in this copolymer substrate.[42] These results, together with the previously-reported chemical analysis,[32] argue that the observed flow is not due to the presence of an impurity such as low molecular weight free PDMS. Details of the chemical analysis will be published.[43] The observations of substrate creep flow reported in this study and in previous investigations[33,34] are consistent with the viscous nature of the mobile phase. Thus, for this specific system, the experimental observations do not necessarily indicate that the bulk yield stress of the copolymer substrate (measured by an Instron tensile test) has been exceeded in the contact region. Nevertheless, the latter mechanism may be entirely plausible for explaining similar creep phenomena involving homogeneous viscoelastic substrates.

CONCLUSIONS

Time-dependent SEM experiments confirmed a plastic flow mechanism proposed in an earlier investigation for the creep of a soft polyester-polydimethylsiloxane block copolymer substrate over higher modulus gold and polystyrene microparticles contacting its surface. The flow process was retarded by the conductive gold/palladium

coating evaporated on the surface shortly after the particle deposition step. Distinct features developed on the conductive coating surface with time. They may have been caused by a contraction of the coating during the flow of the underlying substrate.

The works of adhesion, calculated using the Maugis-Pollock model of adhesion,[14] were found to be approximately $0.041\,J/m^2$ for the gold particles contacting the substrate and $0.022\,J/m^2$ for the polystyrene particles on the same substrate. The contact meniscus heights, measured from the micrographs, were too large to be explained by a linear elastic response to the stresses in the contact regions but were consistent with predictions which assumed the occurrence of plastic deformations.

Acknowledgements

The authors would like to thank Z. Pierce for preparing the polystyrene beads used in this study. We also would like to thank Dr. T. Tombs for his useful comments.

References

1. B. V. Derjaguin, *Kolloid Z.* **69**, 155 (1934).
2. R. S. Bradley, *Philos. Mag.* **13**, 853 (1932).
3. R. S. Bradley, *Trans. Faraday Soc.* **32**, 1088 (1936).
4. H. Krupp, *Adv. Colloid Interface Sci.* **1**, 111 (1967).
5. K. L. Johnson, K. Kendall and A. D. Roberts, *Proc. Royal Soc. Lond. A* **324**, 301 (1971).
6. J. N. Israelachvili and D. Tabor, *Proc. Royal Soc. Lond. A* **312**, 435 (1969).
7. B. V. Derjaguin, V. M. Muller and Yu P. Toporov, *J. Colloid Interface Sci.* **53**, 314 (1975).
8. D. Tabor, *J. Colloid Interface Sci.* **58**, 2 (1977).
9. D. Tabor, *J. Colloid Interface Sci.* **67**, 380 (1978).
10. B. V. Derjaguin, V. M. Muller and Yu P. Toporov, *J. Colloid Interface Sci.* **67**, 378 (1978).
11. V. M. Muller, V. S. Yushchenko and B. V. Derjaguin, *J. Colloid Interface Sci.* **77**, 91 (1980).
12. D. Maugis and M. Barquins, *J. Phys. D* **11**, 1989 (1978).
13. D. Maugis, in *Microscopic Aspects of Adhesion and Lubrication*, J. M. Georges, Ed. (Elsevier, Amsterdam, 1982), p. 221.
14. D. Maugis and H. M. Pollock, *Acta Metal.* **32**, 1323 (1984).
15. D. Maugis and M. Barquins, *J. Phys. D* **16**, 1843 (1983).
16. M. M. Chaudri and E. H. Yoffe, *Philos. Mag. A* **44**, 667 (1981).
17. H. M. Pollock, P. Shufflebottom and J. Skinner, *J. Phys. D* **10**, 127 (1977).
18. H. M. Pollock, *J. Phys. D* **11**, 39 (1978).
19. M. D. Pashley and D. Tabor, *Vacuum* **31**, 619 (1981).
20. R. Mouginot and D. Maugis, *J. Mater. Sci.* **20**, 4354 (1985).
21. R. Mouginot, *J. Mater. Sci.* **22**, 989 (1987).
22. R. Mouginot, *J. Am. Ceram. Soc.* **71**, 658 (1988).
23. L. P. DeMejo, D. S. Rimai and R. C. Bowen, *J. Adhes. Sci. Technol.* **2**, 331 (1988).
24. D. S. Rimai, L. P. DeMejo and R. C. Bowen, *J. Appl. Phys.* **65**, 755 (1989).
25. R. C. Bowen, D. S. Rimai and L. P. DeMejo, *J. Adhes. Sci. Technol.* **3**, 623 (1989).
26. L. P. DeMejo, D. S. Rimai and R. C. Bowen, in *Particles on Surfaces 2: Detection, Adhesion and Removal*, K. L. Mittal, Ed. (Plenum Press, New York, 1989), p. 49–58.
27. D. S. Rimai, L. P. DeMejo and R. C. Bowen, *J. Appl. Phys.* **66**, 3574 (1989).
28. D. S. Rimai, L. P. DeMejo and R. C. Bowen, *J. Appl. Phys.* **68**, 6234 (1990).
29. D. S. Rimai, L. P. DeMejo, W. Vreeland, R. Bowen, S. R. Gaboury and M. W. Urban, *J. Appl. Phys.* **71**, 2253 (1992).
30. R. C. Bowen, L. P. DeMejo, D. S. Rimai and W. B. Vreeland, *J. App Phys.* **70**, 3360 (1991).
31. L. P. DeMeio, D. S. Rimai and R. C. Bowen, *J. Adhes. Sci. Technol.* **5**, 959 (1991).
32. D. S. Rimai, L. P. DeMejo, W. B. Vreeland, R. C. Bowen, S. R. Gaboury and M. W. Urban, *J. Appl. Phys.* **73**, 668 (1993).
33. L. P. DeMejo, D. S. Rimai, J. Chen and R. C. Bowen, *J. Adhesion* **39**, 61 (1992).
34. J. K. Vrtis, C. D. Athanasiou, R. J. Farris, L. P. DeMejo and D. S. Rimai, submitted to *J. Adhes. Sci. Technol.*, in press.

35. M. K. Chaudhury and G. M. Whitesides, *Langmuir* **7**, 1013 (1991).
M. K. Chaudhury and M. J. Owen, *J. Phys. Chem.* **97**, 5722 (1993).
36. D. S. Rimai, R. S. Moore, R. C. Bowen, V. K. Smith and P. E. Woodgate, *J. Mater. Res.* **8**, 662 (1993).
37. L. N. Rogers and J. Reed, *J. Phys. D* **17**, 677 (1984).
38. J. Reed, in *Particles on Surfaces 2: Detection, Adhesion, and Removal*, K. L. Mittal, Ed. (Plenum Press, New York, 1989), p. 3–17.
39. S. Wall, W. John and S. L. Goren, in *Particles on Surfaces 2: Detection, Adhesion, and Removal*, K. L. Mittal, Ed. (Plenum Press, New York, 1989), p. 19–34.
40. D. W. Van Krevelen, Ed., *Properties of Polymers* (Elsevier, Amsterdam, 1990).
41. A. Gent, Private communication, 1991.
42. T. H. Mourey, Private communication, 1992.
43. T. H. Mourey, J. Chen, L. DeMejo, R. C. Bowen and D. S. Rimai, to be published.