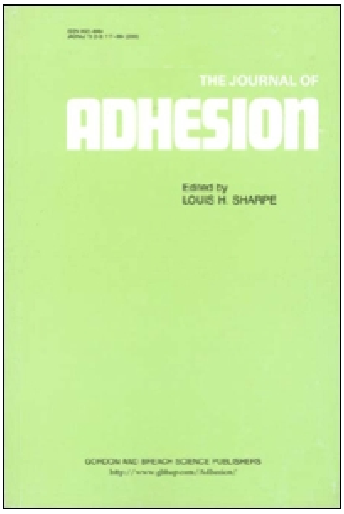

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Time-Dependent Adhesion-Induced Phenomena: Viscoelastic Creep of a Substrate Polymer Over Rigid Particles

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The adhesion of micrometer-size particles to an alternating block copolymer composed of polydimethylsiloxane and polyester was found to be accompanied by substantial viscoelastic flow of the substrate polymer. This flow gave rise to contact radii, which were substantially larger than those predicted by the JKR theory. Moreover, tensile-induced creep of the substrate resulted in anomalously large menisci that actually flowed up several particle heights. The flow of the material occurred over a period of days and, in some instances, the observed contact radii were greater than a critical radius for substantial engulfment of the particles by the substrate. Craters were left behind after particle removal, suggesting plastic-rather than elastic response of the substrate polymer to the surface-force-induced stresses. Size-exclusion chromatography has identified the presence of lower molecular weight polydimethylsiloxane-rich copolymer species in the *n*-hexane soluble mobile phase responsible for the unexpected behavior exhibited by this polymer substrate.

Keywords: Polyester; polydimethylsiloxane; block copolymer; creep; surface forces; plastic deformation; adhesion-induced phenomena; size-exclusion chromatography; ultraviolet absorption detector; differential refractive index detector

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INTRODUCTION

Particle adhesion to surfaces has been the subject of investigation for over sixty years. Derjaguin [1] and Bradley [2, 3] originally postulated, independently, that significant stresses can result from surface forces and give rise to the deformations observed between contacting materials. Derjaguin [1] calculated the contact radius between a particle and a substrate by assuming that the particle could be treated as a Hertzian indentor. As a result, the contact radius, a, was related to the initial, loading force, F^0, the particle radius, R, and the Young's modulus and Poisson's ratio of the substrate, E and ν, respectively, according to

$$a^3 = (3/4)\, F^0 R\, [(1-\nu^2)/E] \tag{1}$$

The loading force, in turn, was assumed to arise from van der Waals interactions [4] such that

$$F^0 = \hbar\varpi\, R/(8\pi z_0^2) \tag{2}$$

where $\hbar\varpi$ is the Hamaker coefficient and z_0 is the separation distance between the two materials. Substituting Equation (2) into Equation (1) yielded

$$a^3 = [(3\hbar\varpi R^2)/(32\pi z_0^2)]\, [(1-\nu^2)/E] \tag{3}$$

The fact that surface-force-induced stresses could be large enough to exceed the elastic limit of at least one of the interacting materials was first recognized by Krupp [4]. He introduced a phenomenological model that subdivided the contact zone into a plastically deformable, high stress, inner circular region and a lower stress, elastic, outer annular region. Plasticity was described by assuming a time-dependent hardness parameter and allowing only compressive stresses.

Johnson, Kendall and Roberts [5] measured the contact radius between macroscopic gelatin and rubber spheres and found it to be approximately double that predicted by Derjaguin's model. Assuming linear elastic response of the materials, they proposed a model (hereafter referred to as the JKR theory), which characterized the nature of the interaction between contacting bodies as compressive toward the center of the contact zone and tensile in the outer regions of contact. Thus, the contact radius dependence on the particle radius, the thermodynamic work of adhesion, w_A, and any externally applied load, P, was expressed as

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

w_A is related to the surface free 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

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

where

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

and ν_i and E_i are the Poisson's ratio and Young's modulus of the i^{th} material. If one material is significantly more compliant than the other, as is the case for the copolymer substrate investigated in this study, and the rigid particles are not subjected to any external loads, then the JKR theory predicts that

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

where ν is the Poisson's ratio of the more compliant material.

Tabor [6] showed that the height of the meniscus, h, around a rigid particle contacting an elastic material could be approximated using the JKR model by

$$h = \{[R(w_A/2)^2]/E^2\}^{1/3} \tag{9}$$

Maugis and coworkers [7–10] introduced a material hardness parameter, H, which they equated to three times the yield strength, Y, of the material in their approach to expand the JKR theory to include non-recoverable plastic flow. For the case of total plasticity, Maugis and Pollock [10] showed that, in the presence of an applied load, P,

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

and for the special case of zero applied load, which is relevant to this work, equation (10) simplifies and rearranges to yield

$$a^2 = (2w_A R)/(3Y) \tag{11}$$

for the contact radius dependence on the particle radius.

Experimental observations of adhesion-induced deformations between micrometer-size particles and substrates, using a scanning electron microscope (SEM), have led to the determination of the power law dependences of the contact radii on the particle radii or Young's moduli of the interacting materials [11–18]. These results, viewed in the context of the aforementioned models, have enabled Rimai and coworkers to distinguish between elastic and plastic deformations for different particle/substrate systems [15, 16]. The surface force apparatus and the atomic force microscope have also been utilized to measure surface forces, adhesion-induced contact radii, and meniscus heights, which have complemented the SEM studies [17–19].

Recent investigations by Chaudhury [20–22], DeMejo and coworkers [23], and Vrtis and coworkers [24], focused on adhesion hysteresis and adhesion-induced interfacial creep of polydimethylsiloxane (PDMS)-rich materials. The adhesion energies of semispherical lenses and flat sheets of elastomeric PDMS chemically modified by chemisorption of hydrolyzed hexadecyltrichlorosilane were estimated by Chaudhury and coworkers from load- and unload-deformation experiments. They measured the deformations at random intervals after each load reached a steady value. The observed adhesion hysteresis was attributed to surface heterogeneities or defects in the monolayer structures rather than interdigitation of the monolayer alkyl chains.

Anomalously large contact menisci, interparticle bridging and particle encapsulation, due to the adhesion-induced flow of a soft polyester/PDMS copolymer substrate over micrometer- and submicrometer-size spherical particles, have been observed by DeMejo and coworkers [23] with a scanning electron microscope. The observations were usually made at least one week after the particles were deposited on the substrate. The height of the menisci and the size of the contact radii were well in excess of those predicted by small deformation linear elastic theories, such as the JKR theory [5, 6]. 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/PDMS copolymer substrate and gold or tin particles, were observed by Vrtis and coworkers [24] after these particles were removed by amalgamation with mercury. These observations further supported the plastic flow mechanism proposed to explain the original results.

If the deformations were plastic in nature, characteristic times associated with yielding or creep should be observable. Time-dependent adhesion-induced phenomena have both been postulated and experimentally observed [4, 13, 20–26]. In a recent study, a time dependence of the contact radius was demonstrated for micrometer-size gold and polystyrene particles in contact with the aforementioned polyester/PDMS substrate [26].

In this paper, the major observations and conclusions of the previous investigations of particles contacting the polyester/PDMS substrate are reviewed. In addition, more detailed analytical data are presented that characterize the chemical and molecular structure of the mobile phase in the substrate. This hexane soluble, PDMS-rich phase was shown previously to give rise to the anomalous adhesion-induced viscoelastic creep behavior [26].

EXPERIMENTAL PROCEDURE

The polyester/PDMS copolymer substrate film was cast out of a 14.5% solution in methylene chloride onto a Teflon surface. This substrate film was a polyester/polydimethylsiloxane block copolymer (synthesized in our laboratory) which contained alternating blocks of polyester and polydimethylsiloxane, as described in a previous investigation [23]. Each set of particles listed in Table I were deposited onto the smoother (air/polymer interface) side of the film by gently sprinkling them from a height of approximately 1 cm. This avoided significant contributions to the size of the contact radii due to the kinetic energy

TABLE I Particle and substrate characteristics

Materials	*Average particle Radius* (μm)	*Young's Modulus* (N/m^2)
Gold	1.3	8×10^{10}
Glass	3.6	6×10^{10}
Tin	1.5	4×10^{10}
Polystyrene	0.5, 2.2, 3.6	3×10^{9}
Poly(vinylidene fluoride)	0.2	1×10^{9}
Polyester/PDMS	–	9×10^{6}

of the particle [27,28]. The measured average radii [23–26] and Young's moduli [29,30] (literature values) of these particles and the modulus of the substrate (as determined using an Instron tensile tester) [23] are shown in Table I.

The gold and tin particles, which had broad size distributions and were spheroidal in shape, were obtained from ALFA Chemicals, Inc. The glass microspheres were obtained from Duke Scientific Corporation. The poly(vinylidene fluoride) particles were purchased from the Pennwalt Corporation under the trade name of Kynar 301F™. The polystyrene beads were produced in-house [23,26]. The Young's moduli of all the particles listed in Table I are at least two orders of magnitude larger than that of the substrate. Assuming material homogeneity, this large modulus difference implies that only the substrate material would be expected to deform in the contact zone.

In order to determine the mobile phase of the subtrate, 1 gram of the polyester/PDMS film was extracted with four 20 mL portions of high pressure liquid chromatography (HPLC)-grade 97% *n*-hexane. The extracts were combined, blown to dryness with a stream of nitrogen and weighed. The average weight percent extracted for two trials was $6.7 \pm 0.3\%$.

The copolymer substrate before and after *n*-hexane extraction as well as the *n*-hexane extract were analyzed by size-exclusion chromatography (SEC). The SEC eluent was HPLC-grade toluene continuously sparged with helium. Three 7.5 × 300 mm Mixed-B columns from Polymer Laboratories, Ltd., thermostated at 30.0°C were used with a nominal eluent flow rate of 1.00 mL/min. The actual flow rate was calculated from the retention volume of a flow marker, 1-chloro-2,4-dinitrobenzene, that was added at a concentration of 0.01% to each sample. Polymer samples were injected in 100 μL at a concentration of 1.5 mg/mL. Ultraviolet (UV) absorption and differential refractive index (DRI) detectors were coupled in series after the columns.

The SEM equipment and procedure used to prepare the samples for viewing at high magnification and high tilt angles have already been described [23–26]. These instruments and procedures allowed the careful examination of the particle/substrate interface both prior to and post-particle removal or solvent extraction of the substrate.

RESULTS AND DISCUSSION

SEM Studies

Large menisci, interparticle bridging and particle encapsulation have been observed when 3.6 micrometer radius glass particles, 2.2 and 3.6 micrometer radius polystyrene particles and 0.2 micrometer radius poly(vinylidene fluoride) particles were deposited on the polyester/PDMS copolymer cast film substrate [23, 26]. Examples of each are shown in Figures 1A, 1B and 1C, respectively.

In Figure 1B the "adhesive" material originating from the substrate was observed to flow up several particle heights. Also, both the isolated smaller poly(vinylidene fluoride) beads and the particle clump (Fig. 1C) appear to be completely encapsulated by the substrate material, and the individual particles appear to sink even deeper into the substrate. In essence, the observed contact radii are greater than a critical radius for substantial engulfment of the particles by the substrate [23].

Figures 2A and 2B are 60° tilt angle scanning electron micrographs of gold and tin particles contacting the polyester/PDMS substrate. The adhesion-induced contact radii appear comparable with the particle radii and, in Figure 2A, large menisci, arising from the tensile interactions between the gold particles and the substrate, are again evident. Interparticle bridging is also apparent among the tin particles in Figure 2B.

Figures 3A and 3B are similar micrographs of the substrates after the gold and tin particles, respectively, were removed. Craters are left in the areas once contacted by the gold and tin particles. The particle removal was accomplished by immersing the samples in mercury for

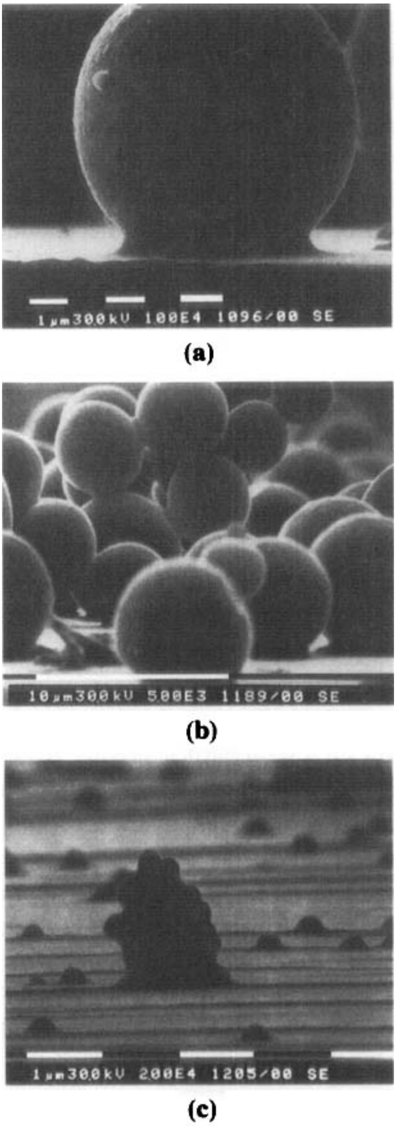
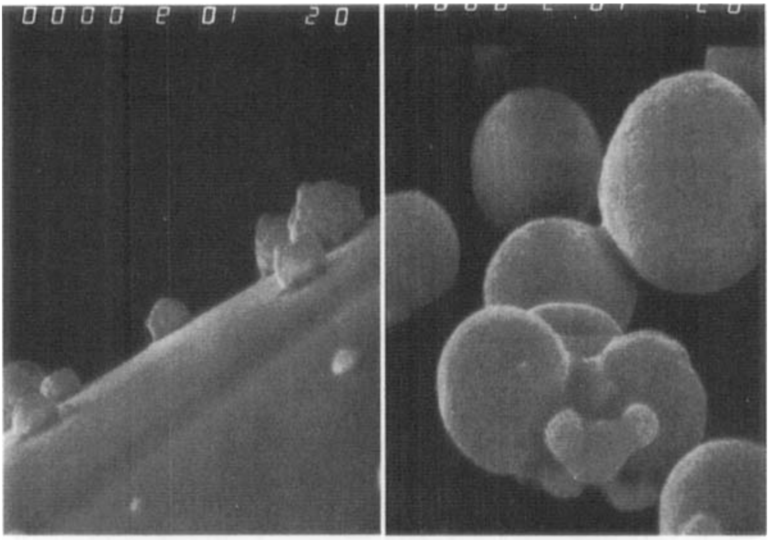


FIGURE 1 SEM micrographs of a 3.6 micrometer radius glass microsphere (1A), 3.6 micrometer radius polystyrene beads (1B), and 0.2 micrometer radius poly(vinylidene fluoride) particles (1C) on the same polyester/PDMS copolymer substrate. Large contact menisci (1A), interparticle bridging even on the third tier of a particle stack (1B), and particle encapsulation by "adhesive" material from the substrate (1C) are clearly detected. Appropriate magnification scales are shown.



(a) (b)

FIGURE 2 Micrographs of 1.3 micrometer radius gold particles (2A) and 1.5 micrometer radius tin particles (2B) on the polyester/PDMS copolymer substrate, as viewed with an SEM at a 60° tilt angle.

periods up to four days and subsequently following controlled procedures to remove any traces of mercury left on the substrate [24]. Control substrates without particles were also processed in a similar manner and did not show any crater formation [24].

Micrographs of the same areas shown in Figure 3 taken a week later did not exhibit significant changes in the size of the craters or the height of the ridges around the craters as discussed in an earlier investigation [24]. These observations suggest that the tensile interactions were sufficient to give rise to plastic rather than elastic flow of the substrate polymer.

Figures 4 and 5 show the time-dependent creep behavior of polymer from the unextracted polyester/PDMS substrate over the polystyrene and poly(vinylidene fluoride) particles and the notable absence of such behavior in the hexane-extracted substrate.

Figure 6 highlights the presence of proiminent surface features (surface ripples) on the unextracted polyester/PDMS substrate and

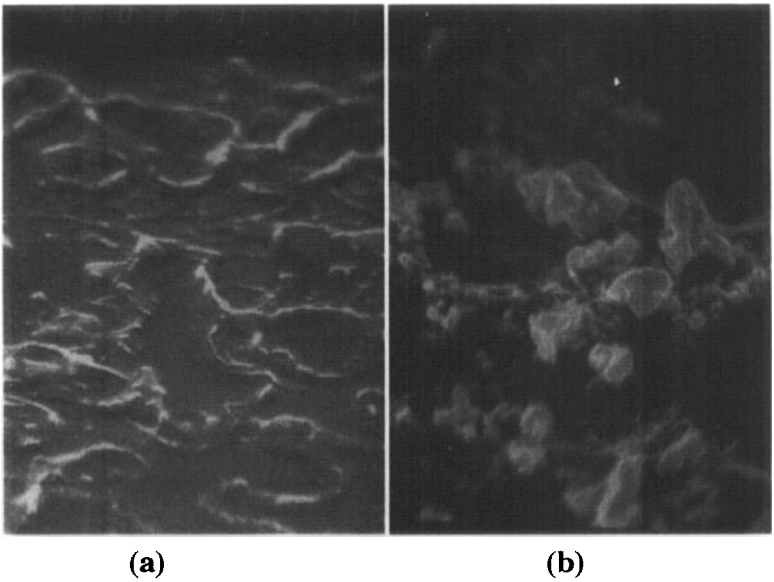
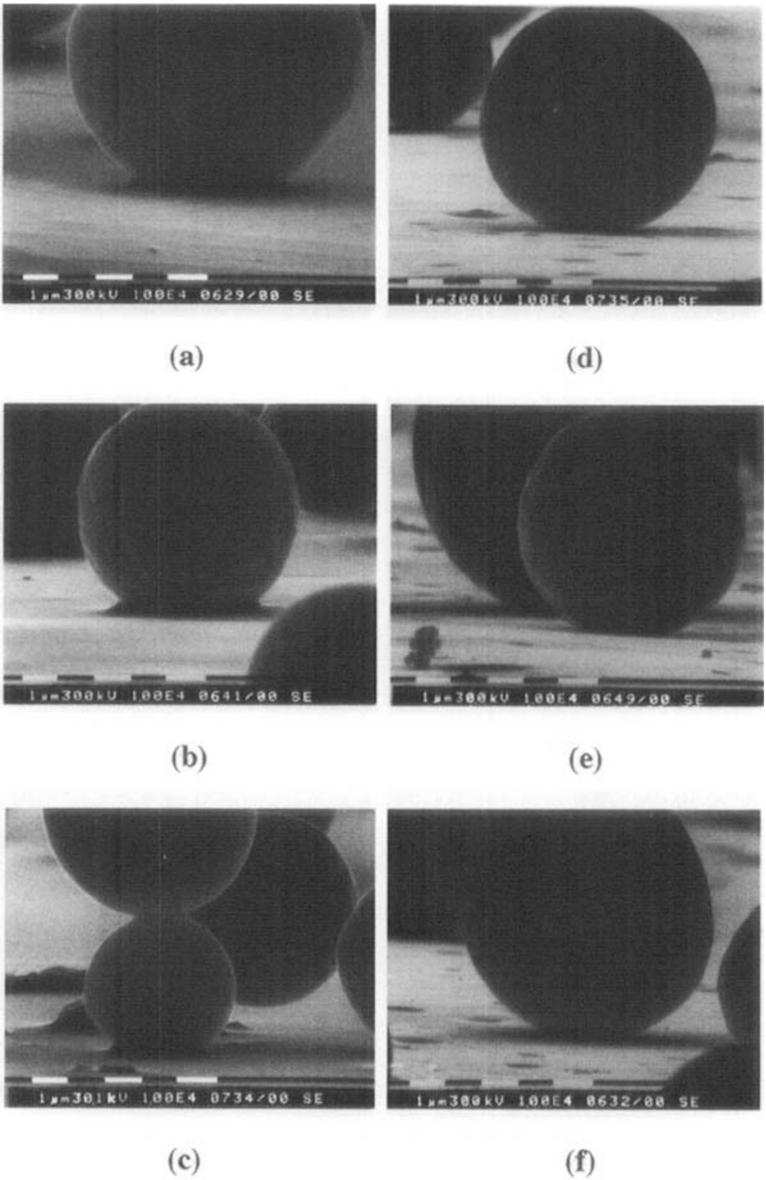


FIGURE 3 SEM micrographs of the polyester/PDMS substrate after the gold (3A) and tin (3B) particles were removed by dissolving them in mercury. Craters of comparable size with the particles are left in the regions where the particles contacted the substrate. Large ridges around the craters are also observed. (Reference 24).

cavities on the hexane-extracted substrate in contact with the poly(vinylidene fluoride) particles.

The contact radius, a, and the height of the meniscus, h, in Figures 4D, 4E, and 4F are approximately 1.5×10^{-8} m and 6×10^{-8} m and 6×10^{-8} m, respectively, in agreement with the JKR model (Equation (8)) and Tabor's prediction (Equation (9)) for a rigid particle contacting an elastic substrate. However, a and h in Figures 4A, 4B and 4C are much larger than the JKR and Tabor predictions, consistent with the presence of a mobile phase in the untreated substrate capable of yielding in response to adhesion-induced surface forces.

Prominent surface features are observed in Figure 6 on both the unextracted polyester/PDMS substrate and the hexane-extracted polyester/PDMS substrate. If the sample is viewed shortly after the conductive coating is applied (Fig. 6C) the surface is ill-defined and no distinct surface features are observed. However, if the samples are viewed one month after the conductive coating is applied (Figs. 6A and 6B) the

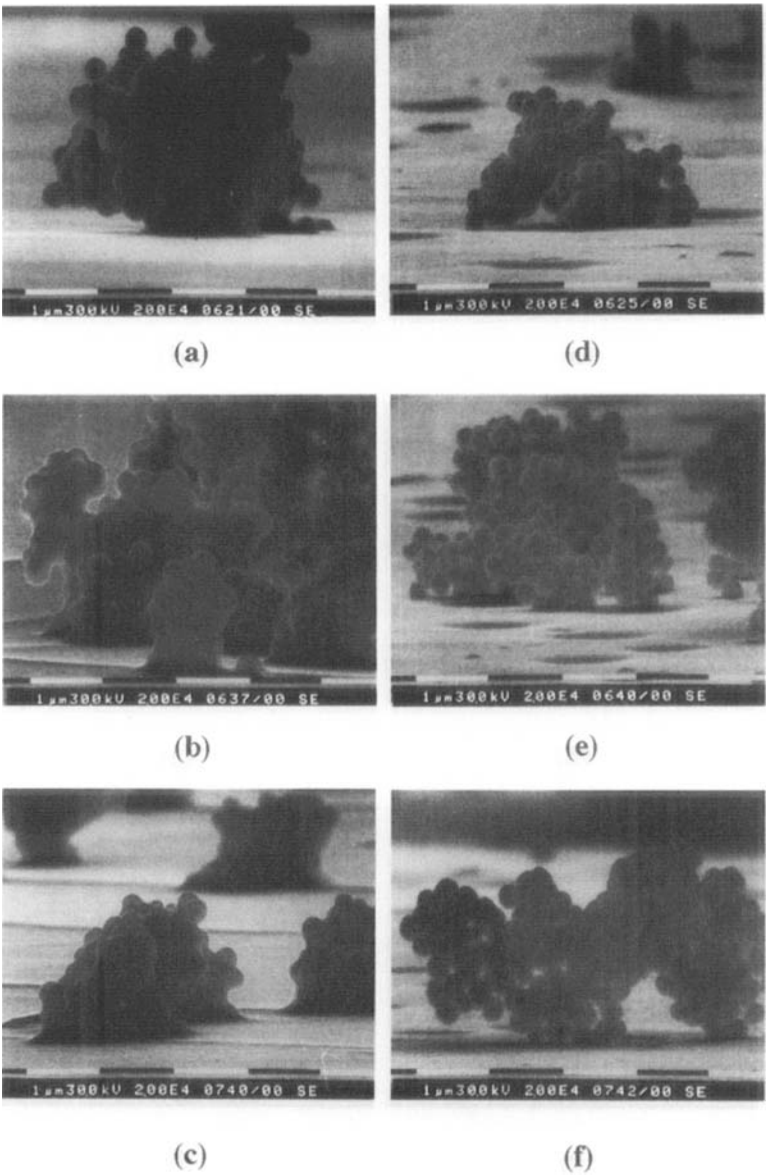


(a) (d)

(b) (e)

(c) (f)

FIGURE 4 SEM micrographs of polystyrene particles fifteen minutes after deposition, one day after deposition, and three days after deposition on the unextracted polyester/PDMS substrate (4A, 4B and 4C, respectively) compared with the same time intervals after deposition on the hexane-extracted polyester/PDMS substrate (4D, 4E, and 4F, respectively).



(a) (d)

(b) (e)

(c) (f)

FIGURE 5 SEM micrographs of poly(vinylidene fluoride) particles fifteen minutes after deposition, one day after deposition, and three days after deposition on the unextracted polyester/PDMS substrate (5A, 5B, and 5C, respectively) compared with the same time intervals after deposition on the hexane-extracted polyester/PDMS substrate (5D, 5E, and 5F, respectively).

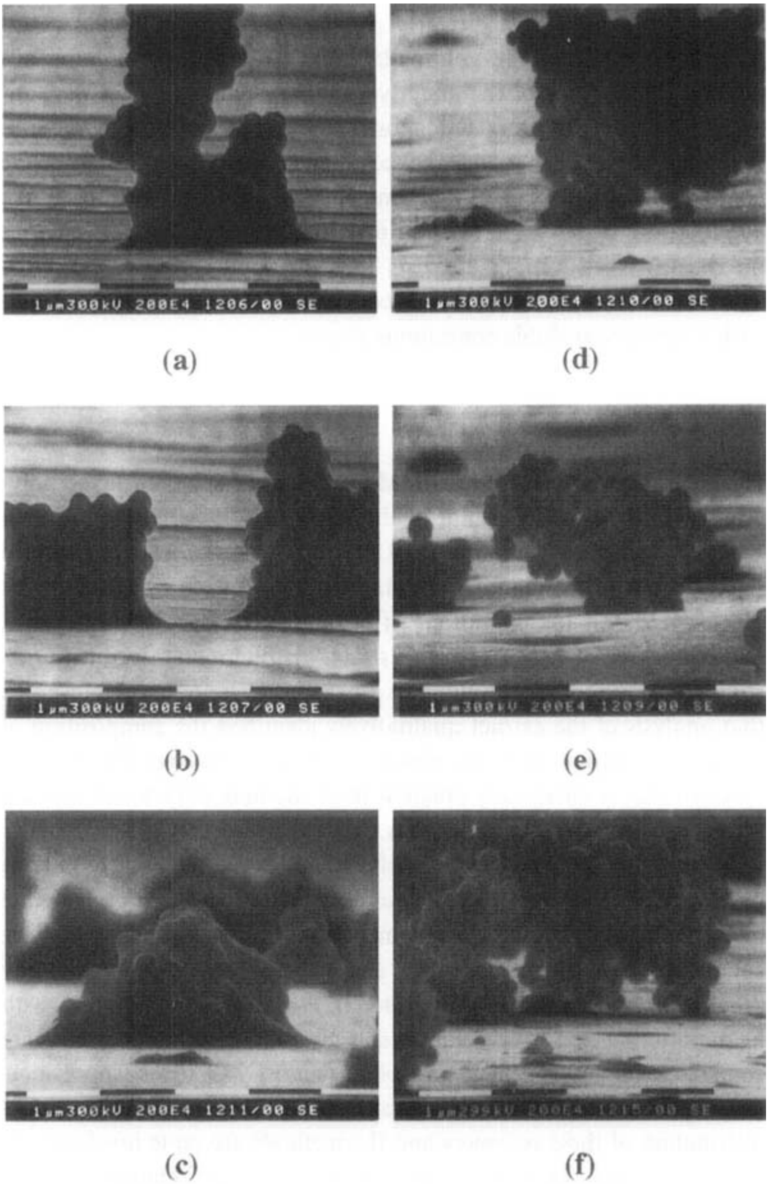


FIGURE 6 SEM micrographs of poly(vinylidene fluoride) particles deposited and coated on the same day but viewed a month later (6A and 6B) or deposited on one day but coated and viewed a month later (6C) on the unextracted unextracted polyester/PDMS substrate compared with the same time intervals after deposition on the hexane-extracted polyester/PDMS substrate (6D, 6E, and 6F, respectively).

substrate surface appears clearly rippled. The surface ripples result from contraction of the gold/palladium coating caused by the adhesion-induced flow of the underlying mobile component of the substrate. The hexane-extracted substrate exhibits prominent cavities regardless of whether it is examined immediately after the conductive coating is applied (Fig. 6F) or one month after application of the conductive coating (Figs. 6D and 6E). The presence of many cavities on the extracted surface suggests that the mobile species from the substrate is the hexane-soluble discontinous phase of a polymer blend with a hexane-insoluble continuous phase.

SEC Analysis

Hexane is a good solvent for PDMS and a poor solvent for the polyester. An extraction of a film of the block copolymer substrate with *n*-hexane is expected to remove PDMS-rich material from the surface selectively. Further removal of soluble material from the bulk of the film depends on the conditions of hexane extraction, film thickness, and the degree of swelling. In this study, the film maintained its integrity and exhibited little swelling in *n*-hexane. Therefore, it is presumed that analysis of the extract qualitatively identified the composition of the material primarily at the surface of the free-standing film. Surface material that is chemically different from the bulk may be anticipated for compositionally heterogeneous copolymers.

A variety of liquid chromatographic fractionation methods have been developed to profile compositional distributions [31]. Poly (methyl methacrylate)/PDMS graft copolymers have been cross-fractionated by combined liquid chromatography and size-exclusion chromatography (SEC) with Fourier transform infrared (FTIR) detection [32]. SEC with light-scattering and concentration detection has been used to measure compositional heterogeneity in polystyrene/PDMS block copolymers [33, 34]. These methods are designed to profile the entire compositional distribution of these polymers and the methods are quite involved and time-consuming. However, such quantitative fractionation schemes are not necessary to identify the mobile surface component of the polyester/PDMS copolymer.

A fundamentally different and less complicated procedure was followed, which takes advantage of the unique and selective responses of differential refractive index (DRI) and ultraviolet absorption (UV) detectors for each block component. The specific refractive index increment (*dn*/*dc*) of polyester is positive in toluene, whereas the *dn*/*dc* of PDMS in toluene is negative. The *dn*/*dc* of a copolymer of the two components is, to a first approximation, linearly proportional to the weight fractions and specific refractive index increments of the individual components. In this example, the *dn*/*dc* of the copolymer is slightly negative in toluene and the DRI response in Figure 7 is therefore negative (the copolymer elutes in the region of the chromatogram before the system peaks in curve *a*). Molecular size decreases with increasing retention volume in SEC chromatograms and the low molecular weight material between 24–30 mL produces a negative DRI response. After extraction with *n*-hexane, the low molecular weight region of the chromatogram (again, between 24–30 mL) has a slightly positive DRI response (curve *b*), indicating an enrichment of the polyester component in this fraction. The material extracted by *n*-hexane (curve *c*) produces a negative DRI response, confirming that the material removed from the film is PDMS-rich and the shift to longer retention volumes is consistent with low molecular weight material.

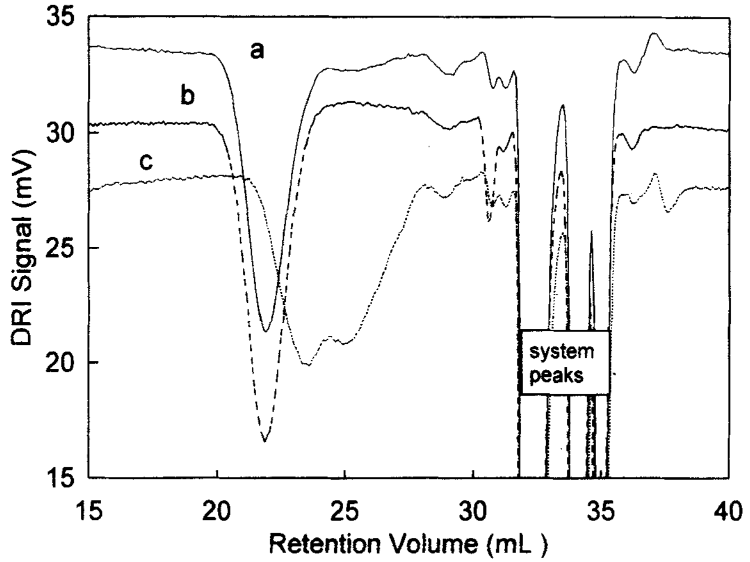


FIGURE 7 SEC-DRI chromatograms in toluene: a – whole polyester/PDMS copolymer; b – copolymer film after extraction with *n*-hexane, c – *n*-hexane extract of copolymer film.

The composition of the extract is confirmed by the UV chromatograms. The polyester component absorbs UV light at 313 nm but the PDMS segment is transparent. The area under the UV chromatogram of the extract in Figure 8 (lower solid trace) is much smaller than the UV response for a comparable amount of the block copolymer (upper dotted trace). The UV absorption of the extract is small but significant since it distinguishes the soluble material as PDMS-rich copolymer rather than PDMS homopolymer.

No significant differences in bulk physical and mechanical properties of the elastomeric substrate were observed before and after the hexane extraction. Since the extracted polymer was lower in molecular weight and rich in polydimethylsiloxane it was expected to exhibit a lower glass transition temperature. After the hexane extraction, as shown in Figures 4D, 4E, 4F 5D, 5E, 5F, 6D, 6E, and 6F, the substrate did not exhibit the original viscoelastic creep behavior. This clearly implicates the hexane-soluble polymer as the species responsible for the observed time-dependent adhesion-induced phenomena.

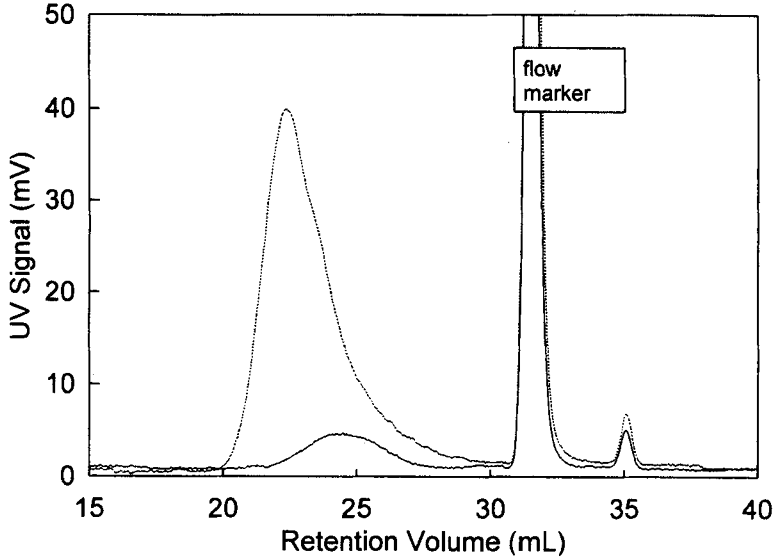


FIGURE 8 SEC-UV chromatograms at 303 nm: upper dotted curve – whole polyester/PDMS copolymer; lower solid curve – *n*-hexane extract of copolymer film.

CONCLUSIONS

The plastic deformation of a mobile phase in a polyester/PDMS substrate in contact with gold, tin, polystyrene, and poly(vinylidene fluoride) particles has been demonstrated by a series of time-dependent SEM experiments. Time-dependent creep phenomena and prominent surface ripples were observed on the unextracted substrate in contact with the particles. On the ohter hand, no evidence of substrate material creep and numerous cavities were observed on the hexane-extracted substrate in contact with the particles. These observations suggest that the conductive gold/palladium coating contracts in response to the adhesion-induced flow of the underlying mobile component and that the mobile component is the discontinuous phase of a polymer blend. A lower molecular weight, hexane-soluble, PDMS-rich copolymer fraction was analyzed by SEC to be the phase responsible for the anomalous creep interaction with each set of particles.

References

[1] Derjaguin, B. V., *Kolloid Z.* **69**, 155 (1934).

[2] Bradley, R. S., *Philos. Mag.* **13**, 853 (1932).

[3] Bradley, R. S., *Trans. Faraday Soc.* **32**, 1088 (1936).

[4] Krupp, H., *Adv. Colloid Interface Sci.* **1**, 111 (1967).

[5] Johnson, K. L., Kendall, K. and Roberts, A. D., *Proc. Royal Soc. Lond. A* **324**, 301 (1971).

[6] Tabor, D., *J. Colloid Interface Sci.* **58**, 2 (1977).

[7] Maugis, D. and Barquins, M., *J. Phys. D* **11**, 1989 (1978).

[8] Maugis, D., in *Microscopic Aspects of Adhesion and Lubrication*, Georges, J. M., Ed. (Elsevier, Amsterdam, 1982), p. 221.

[9] Maugis, D. and Barquins, M., *J. Phys. D* **16**, 1843 (1983).

[10] Maugis, D. and Pollock, H. M., *Acta Metal.* **32**, 1323 (1984).

[11] DeMejo, L. P., Rimai, D. S. and Bowen, R. C., in *Particles on Surfaces2: Detection, Adhesion and Removal*, Mittal, K. L., Ed. (Plenum Press, New York, 1989), pp. 49–58.

[12] Rimai, D. S., DeMejo, L. P. and Bowen, R. C., *J. Appl. Phys.* **68**, 6234 (1990).

[13] Bowen, R. C., DeMejo, L. P., Rimai, D. S. and Vreeland, W. B., *J. Appl. Phys.* **70**, 3360 (1991).

[14] DeMejo, L. P., Rimai, D. S. and Bowen, R. C., *J. Ahes. Sci. Technol.* **5**, 959 (1991).

[15] Rimai, D. S., DeMejo, L. P., Vreeland, W., Bowen, R., Gaboury, S. R. and Urban, M. W., *J. App. Phys.* **71**, 2253 (1992).

[16] Rimai, D. S., DeMejo, L. P., Vreeland, W., Bowen, R., Gaboury, S. R. and Urban, M. W., *J. Appl. Phys.* **73**, 668 (1993).

[17] Horn, R. G., Israelachvili, J. N. and Pribac, F., *J. Colloid Interface Sci.* **115**, 480 (1987).

[18] Merrill, W. M., Pocius, A. V., Thakker, B. V. and Tirrell, M., *Langmuir* **7**, 1975 (1991).

[19] Schaefer, D. M., Carpenter, M., Reinfenberger, R., DeMejo, L. P. and Rimai, D. S., *J. Adhes. Sci. Technol.* **8**, 197 (1994).

[20] Chaudhury, M. K. and Whitesides, G. M., *Langmuir* **7**, 1013 (1991).
[21] Chaudhury, M. K. and Whitesides, G. M., *Science* **255**, 1230 (1992).
[22] Chaudhury, M. K. and Owen, M. J., *J. Phys. Chem.* **97**, 5722 (1993).
[23] DeMejo, L. P., Rimai, D. S., Chen, J. and Bowen, R. C., *J. Adhesion* **39**, 61 (1992); DeMejo, L. P., Rimai, D. S., Chen, J. H. and Bowen, R. C., in *Particles on Surfaces 4: Detection, Adhesion and Removal*, Mittal, K. L., Ed. (Marcel Dekker, New York, 1995), pp. 33–45.
[24] Vrtis, J. K., Athanasiou, C. D., Farris, R. J., DeMejo, L. P. and Rimai, D. S., *J. Adhes. Sci. Technol.* **8**, 929 (1994).
[25] Krishnan, S., Busnaina, A. A., Rimai, D. S. and DeMejo, L. P., *J. Adhesion Sci. Technol.* **8**, 1357 (1994).
[26] DeMejo, L. P., Rimai, D. S., Chen, J. H. and Bowen, R. C., *J. Adhesion* **48**, 47 (1995).
[27] Rogers, L. N. and Reed, J., *J. Phys.* **D17**, 677 (1984).
[28] Wall, S., John, W. and Goren, S. L., in *Particles on Surfaces 2: Detection, Adhesion, and Removal*, Mittal, K. L., Ed. (Plenum Press, New York, 1989), pp. 19–34.
[29] Van Krevelen, D. W., Ed., *Properties of Polymers* (Elsevier, Amsterdam, 1990).
[30] ASM Handbook (ASM International, Metals Park, OH, 1992), 2, pp. 1116–1117, 1166–1167.
[31] Mourey, T. H. and Schunk, T. C., "Synthetic Polymers" in *Chromatography V*, Heftmann, E., Ed. (Elsevier, Amsterdam, 1992), Chap. 22.
[32] Schunk, T. C. and Long, T. E. (1995). *J. Chromatogr.* **A692**, 221.
[33] Dumelow, T., Holding, S. R., Maisey, L. J. and Dawkins, J. V., *Polymer* **27**, 1170 (1986).
[34] Dumelow, T., *J. Macromol. Sci.-Chem.* **A26**, 125 (1989).