Fracture Behavior of Colloidal Polymer Particles in Fast-Frozen Suspensions Viewed by Cryo-SEM

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ABSTRACT: Cryogenic scanning electron microscopy (cryo-SEM) is a powerful technique of visualizing the state of microstructure, or nanostructure, of colloidal polymer suspensions, or dispersions, after they have been immobilized by fast-freezing and fractured for imaging. The fracture is done at −196 °C, the normal boiling point of liquid nitrogen, which is far below the glass transition temperature of both bulk and fully coalesced particles of the polymers examined. The cryo-SEM images show a range of responses of particles to the fracture that propagated past them through ice: cleanly sliced through, i.e., broken, partially drawn and unbroken, drawn to breakage, and neither drawn nor broken. The drawn particles often display curious features called "pullouts" that have been generated by plastic deformation of parts of the particles that remain in a fracture surface, or sometimes both surfaces near the tip of a fracture that halted. The main morphologies of pullouts are mushroom shaped, spool shaped, and awl shaped. Pullouts form when the molecular weight (M_w) of the polymer exceeds twice the entanglement molecular weight (M_e); they do not form when cross-linking density exceeds a certain level. We hypothesize that nonbulk molecular organization of submicron colloidal particles, perhaps most disturbed in a surface zone, promotes the formation of pullouts. Pullouts have been seen in particles from 500 nm in diameter, the largest examined, down to 30 nm, the smallest. At least when M_w is greater than twice M_e, T_g does not affect the formation of pullouts. The pullout features indicate that the yield behavior, and thus the mechanical properties, of submicron particles synthesized by emulsion polymerization differs from that of polymer crazing in bulk and in thin films; the molecular-level explanation stands as a challenge to macromolecular science.

Introduction

Cryogenic scanning electron microscopy (cryo-SEM) has successfully revealed the morphologies of latex coatings as well as some surfactant/water systems.[1−3] This powerful technique consists of cryo-immobilizing specimens, fracturing them to expose a cross-section, sublimating some of the frozen water that remains in the structure to increase topographic contrast, coating the fracture surface with a thin layer of metal to avoid charging, and then imaging the surface on the cold stage of a high-resolution field emission scanning electron microscope. During the freeze-fracture step, interesting features called "pullouts" can be induced by the plainly plastic deformation of latex particles into partially elongated shapes that usually remain held in the ice of one or the other of the complementary fracture surfaces.

This plastic deformation of polymer particles less than 1 μm in diameter during freeze-fracture was noted in the early 1970s[4,5] in transmission electron microscopy images of freeze-fracture replicas (FFTEM) from biological tissues and from suspensions of polystyrene and polyacrylate latex. In the freeze-fracture TEM technique, a fast-frozen specimen is fractured with a chilled knife that is pressed into the specimen, the fracture surface is shadow-cast with platinum backed by carbon, and then the remaining polymer material is removed to leave a replica film for examination by TEM at room temperature. Other FFTEM images of pullouts were reported by Disanayaka et al.[6] and Sudesh et al.[7,8] Pullouts were noticed by our colleague, Yue Ma, several years ago[9] in high-resolution cryo-SEM images of polystyrene latex suspension fast-frozen at liquid nitrogen temperature (−196 °C). The images of some fracture surfaces inclined to the microscope axis as well as images of tilted specimens showed pullouts clearly. Their lengths were as much as twice the original particle diameter. These features are surprising because the polymer particles were fractured at temperatures far below the glass transition temperature, T_g, of the bulk polymer and so might have been expected to be glassy and brittle. For example, bulk polymer reconstituted by coalescence of polystyrene latex particles about 500 nm in diameter fractures in brittle fashion at −196 °C, whereas when a suspension of the original particles is fast-frozen to that temperature and fractured, many of those held in the fracture surfaces viewed are elongated into pullouts.[9] The T_g of bulk polystyrene is 100 °C.[10]

The reasons for the plastic deformation of latex particles as much as 296 °C below the T_g of the bulk polymer have been controversial since Sleytr and Robards' review.[5] These scientists, as well as Sudesh et al., believed the plastic deformation of the polymer particles is due to heat generated by the fracture process,[7,8] which is highly unlikely because the adiabatic temperature rise of a pullout, owing to work that would be done if the elongating force were always the estimated force to finally break it, we have reckoned to be no more than a few degrees centigrade.

In this paper, we report experiments that captured pullouts in various stages of formation behind arrested fracture tips and on surfaces of complete fractures. The results indicate how pullouts differ with the molecular weight of the polymer chains

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Table 1. Key Features of the Model Latexes[a]

model latex	composition wt %	solids content wt %	particle size nm
F158	100 styrene	41.0	210
C428	100 styrene	41.5	130
C429	99.5 styrene 0.5 BDDA	40.6	130
C430	95 styrene 5 BDDA	39.6	130
F157	85 styrene 15 BDDA	41.3	130
PS3	99.5 styrene 0.5 TDM	41.0	130
PS4	98 styrene 2 TDM	40.7	130
PS5	95 styrene 5 TDM	40.1	130
F193	50 styrene 50 BA	40.1	130
F194	100 BA	40.3	130

[a] BDDA, butanediol diacrylate is a cross-linking agent; TDM, *tert*-dodecyl mercaptan is a chain transfer agent; BA, butyl acrylate.

making up a particle, the particle size, and the bulk T_g. In the light of these results, we infer a scenario of formation of pullouts and draw on the literature for the possible causes, taking account of (i) the mechanism of crazing and fracture in glassy bulk polymers, (ii) the now well-documented crazing and ductile failure of thin films of otherwise glassy polymers on the order of a micron thick, and (iii) the evidence of disturbed molecular organization within a particle owing to the confining influence of its size and the way in which it was produced. Apart from the intrinsic scientific interest they arouse, the pullouts, once regarded as artifacts in cryo-SEM, are useful indicators of competition between adhesion and cohesive failure during crack propagation, as mediated by not only the molecular weight and entanglement length of latex polymers but also interparticle diffusion.[9,11]

Experimental Section

Materials. Ten model latexes were synthesized by a standard semicontinuous emulsion polymerization process; see Table 1. Most of them were polystyrene latexes around 130 nm in diameter with a narrow particle size distribution. Model latexes C429, C430, and F157 were toughened by adding different amounts of cross-linking agent butanediol diacrylate (BDDA) in the synthesis. The molecular weight of polymer chains inside latex particles of PS3, PS4, and PS5 was lowered by adding a small amount of the chain transfer agent *tert*-dodecyl mercaptan (TDM). F158 polystyrene model latex had a larger particle size, 210 nm. F194 was a poly(butyl acrylate) latex and F193 was made of copolymer poly(styrene-*co*-butyl acrylate); these were designed to study the effect of glass transition temperature (T_g) of the latex polymer. All the model latexes contained 1 wt % sodium dodecyl sulfate (SDS) surfactant (Aldrich), based on the amount of monomers, as the electrostatic stabilizer on the particle surfaces.

Cryo-SEM of Latex Suspensions. A drop (about 1 mL) of a latex suspension was sandwiched between two freezing planchettes (type A, Ted Pella, Redding, CA). The assemblage was loaded in a Bal-Tec HPM 010 high-pressure-freezing machine (Bal-Tec AG, Balzers, Liechtenstein) and was frozen at 2100 bar within 7−8 ms. The process sealed the sandwich so that the sample was never contacted by the liquid nitrogen of the opposed freezing jets. The assemblage was unloaded and transferred to a liquid nitrogen container; there, it was fractured by inserting the tip of a cold knife between the rims of the two freezing planchettes. One side of the fractured specimen was mounted in a Gatan 626 cryotransfer stage (Gatan, Pleasanton, CA) at the atmospheric boiling temperature of liquid nitrogen, −196 °C. The mounted specimen was then transferred to a precooled Balzers MED 010 sputtering device (Balzers Union, Balzers, Liechtenstein) against a counter flow of dry nitrogen gas to prevent any invasion of room air with its humidity that would turn to frost. Ice in the frozen specimen was partially sublimated away at −96 °C and 2×10^{-9} bar for 14 min. Platinum in an amount equivalent to 3 nm thickness, as measured by a Balzers QSG 301 quartz crystal thickness monitor device (Balzers Union, Balzers, Liechtenstein), was sputtered on the specimen surface at −115 °C. The specimen was then transferred to a Hitachi S900 in-the-lens field emission SEM (FESEM) (Nissei Sangyo America, Ltd., Rolling Meadows, IL) for examination at a low acceleration voltage of 2 keV and a low probe current of about 10^{-11} A. During the SEM imaging, the sample temperature on the cold stage was kept around −160 °C.

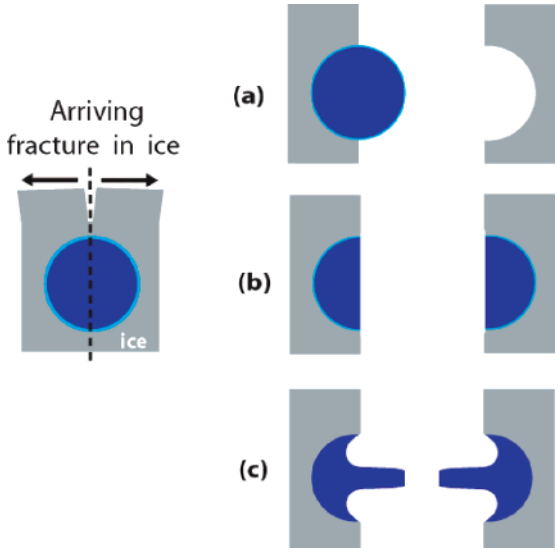

Figure 1. Three main outcomes as a fracture front meets a latex particle in frozen suspension.

Molecular Weight Measurement by Gel Permeation Chromatography (GPC). A drop of suspension of each model latex C428, PS3, PS4, and PS5 was first predried in room air for 1 day and then was further dried under vacuum for one night. The dried specimen was finally dissolved in tetrahydrofuran (THF), and the solution was put into a Waters 590/717/410 GPC machine (Waters, Milford, MA), which determined the molecular weight and molecular weight distribution by calibration with polystyrene standards from Polymer Laboratories Inc.

Results

The Formation Process of Pullouts. The procedure of prying apart the planchette sandwich and thereby generating a crack that runs through the frozen sample takes less than a second, and the rapidly advancing crack is not accessible to view. What has actually happened can only be deduced from the end result, a fracture surface, occasionally with an arrested side fracture, and the physical principles presumed to govern the process. Three outcomes are shown schematically in Figure 1. Scenarios for each are sketched in the next paragraph.

Before fracture, the latex particles in the cryo-immobilized suspension are surrounded by and adhere to vitreous (or extremely polycrystalline) ice from the high-pressure freezing. During fracture, the fracture front, i.e., the crack tip, gets started in ice and, upon encountering a particle, has three main options: Figure 1a, it proceeds through a caplike portion of the particle−ice interface by adhesion failure or local delamination; Figure 1b, it enters and proceeds through the particle, fracturing it by cohesive failure cleanly into two segments, each of which adheres to ice around it on its side of the opening fracture; Figure 1c, it enters the particle near its midriff by plastically developing a dimple that grows circumferentially into

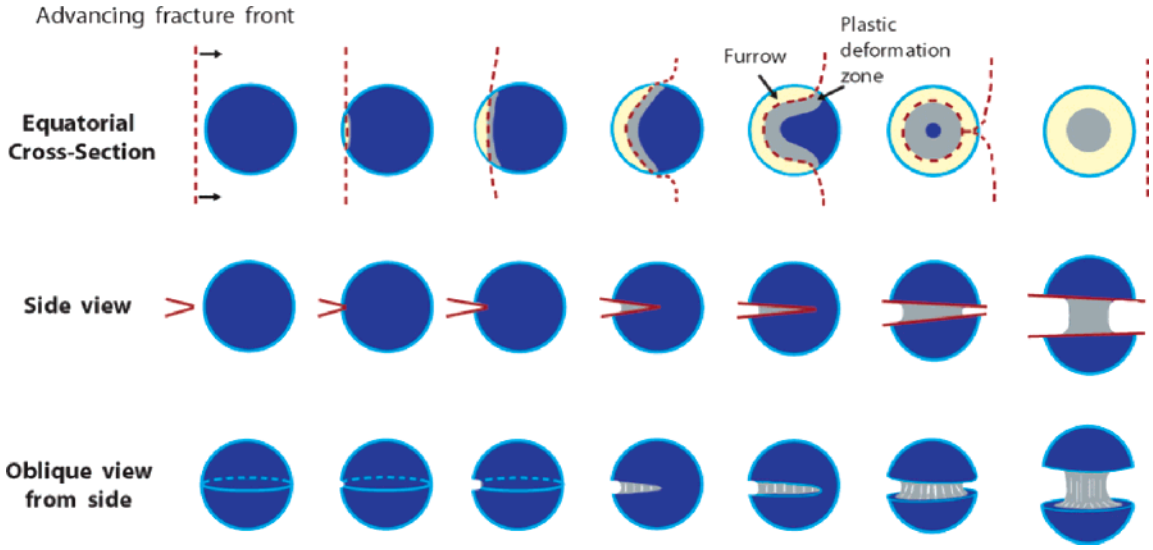

Figure 2. Schematic of early stages of the formation of a pullout as a fracture front advances through frozen suspension, based on evidence in Figure 4 and other similar images. The ice around the particle is transparent here; the gray area in the particle denotes the plastic deformation zone and the yellow area denotes the furrow feature provided by the fracture.

a furrow but, encountering growing resistance of polymer being extended, propagates around a central neck, meeting itself on the far side and proceeding onward into ice beyond. In the second as well as the third option, the strength of adhesion of the particle surface to ice plainly must be enough to prevent local delamination, i.e., to withstand the tensile and shear forces transmitted through the fracturing or extending polymer to its interface with the ice. Cross-sectional views, side views, and oblique side views of the third option are illustrated in Figure 2; we judge it the most likely to account for pullouts.

Figure 3 is a schematic of how three different shapes of pullouts can be formed during advance of a fracture. As the crack tip advances beyond the particle, the crack tends to open more at the particle, subjecting it to tensile strain and a tensile force that tests the strength of adhesion of its still-spherical ends to their ice. If the test is met, the opening crack draws the still-intact neck into an elongating stem that gives the particle a rivet shape. The drawing is surely ductile and accompanied by strain hardening that enables the slimming stem to support its load without breaking. The strain hardening is presumably by some combination of intensification of entanglement of polymer chains and of alignment of chains that can come together. That they do gather into ligaments that are mostly partially fused but occasionally separated by ventilated invaginations (rather than the isolated voids that initiate ordinary crazing in bulk polymer) is sometimes plainly evident in nanocraze-like texture of the stems. As the fracture front propagates further, the crack must open more and more at a given particle, subjecting it to still more tensile strain until the rivet-shaped stem breaks. It can break by some combination of chain scission and disentanglement accompanied by disengagement, i.e., extraction of individual polymer chains. This leaves mushroom-shaped pullouts that adhere to one side of the fracture or the other, i.e., to one of the complementary fracture surfaces; see Figure 3a2.

Or, as the opening crack draws the neck into an elongating one, the tensile load on one of the spherical end caps, likely the smaller if they differ in mere size, may exceed the strength of adhesion of polymer particle to ice, so that the end cap delaminates, i.e., detaches from the ice. This leaves spool-shaped pullouts that adhere to one side of the fracture or the other (Figure 3b2) or sometimes come loose and end up tumbled on the fracture surface.

Or, because one of the spherical end caps is rather smaller, the opening crack may draw the neck into a long-tapered stem that finally breaks; alternatively, it may pull enough polymer out of the end cap to shrink the cap until the load finally exceeds the strength of the cap's adhesion to the ice. This leaves an awl-shaped pullout whose spherical end cap adheres to one side of the fracture or the other (Figure 3c2). These, too, sometimes come loose and end up tumbled. Occasionally, in an image of a fracture surface, a side fracture is seen, the opening of which drew a particle somewhat, but then ceased, leaving a spool-shaped pullout with both end caps still adhering to ice in the two fracture surfaces. Indeed, the drawing of multiple spool-shaped polymer bridges may have been responsible for arresting the side crack before it produced many pullouts of the more common mushroom and awl shapes.

Cryo-SEM images in Figure 4 are examples of the different shapes of pullouts from polystyrene latex particles and acrylic latex particles: Figure 4a shows mushroom-shaped pullouts from polystyrene particles 500 nm in diameter that have tumbled on the fracture surface; Figure 4b is described below; Figure 4e shows awl-shaped pullouts with long conical tips, some of which have tumbled; parts c and d of Figure 4 are serendipitous images of a side fracture in a 5 wt % F158 frozen sample. The side fracture is perpendicular to the main fracture surface and evidently halted. The drawn yet unbroken particles spanning it are evidence of the process by which pullouts form. The plane in which the fracture arrives affects the morphologies of pullouts. When the plane arrives at the equator of a particle, the particle is drawn symmetrically, as was the one in the white box in Figure 4c; otherwise the particle is drawn asymmetrically, as was the one in Figure 4d.

The way the pullouts evolve in shape suggests that, when a fracture tip encounters a particle near its midriff, the opening motion draws the surface zone plastically, causing it to dimple inward as the tip goes on around the particle's core (see Figure 2). Meanwhile, the core is increasingly drawn into a neck as in crazing (Figure 3); as it does so, it develops vestiges of ligaments or fibrils such as can be seen in the micrographs of Figure 4. That process resembles quasibrittle crazing with no need for nucleation, nor for the viscous fingering mechanism of crazing in bulk and in thin film,[13] because the neck is surrounded by void from the outset. It is noteworthy that the pullouts are the

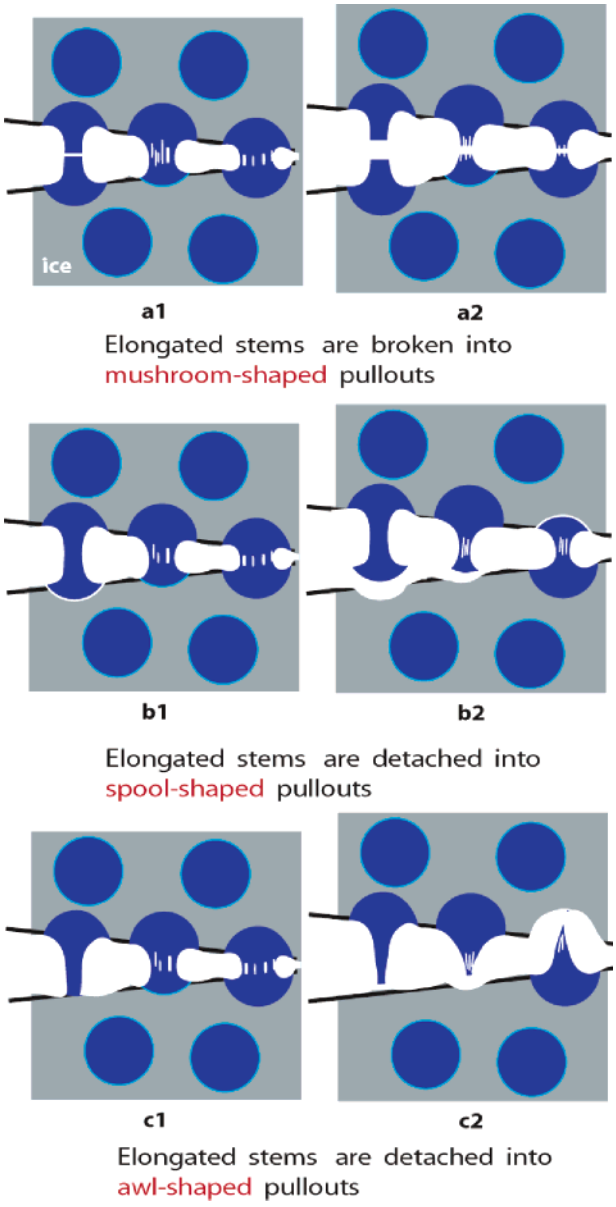

Figure 3. Schematic of likely later stages of development of pullouts as a fracture propagates through frozen suspension. Striations indicate nanocrazing-like texture often seen on stems, shanks, and tips.

results of plastic deformation at the scale of single fibrils in crazing of thin polymer film; the latter is reported as 10−150 nm.[13]

The volumes of drawn particles may be indicators of the drawing process. With the software AutoCAD 2004 (Autodesk PSG), the volumes of the spools in the white boxes in Figure 4 were estimated on the assumption that they are axially symmetric and so can be modeled by revolving their two-dimensional image through 180°. The volume of the spool as a body of revolution with the cross-section seen in the image was compared with the volume of a sphere with the average radius of the arcs-of-circle of the cross-sections of the end caps. As shown in Table 2, the volume of the spool in Figure 4c is apparently 6% larger than the volume of its original particle and that of the spool in Figure 4d is 21% larger than its original particle volume. The error of the estimates seems unlikely to be as much as 21%. The volume may actually grow during drawing because ventilated invaginations, or grooves, and perhaps occasional interior voids, appear on stems, as suggested in Figure 3a. This supposition is buttressed by the images in parts f and g of Figure 4, which show the longitudinal crazelike texture on the pullouts clearly. Figure 4b shows the radial crazelike texture on the annular surfaces of mushroom-shaped pullouts.

Effect of Molecular Weight on Pullouts. Changing molecular weight (M_w) of latex particles affects the morphologies of pullouts. In bulk material, stable crazes usually do not form if M_w is less than twice the critical molecular weight for entanglement (M_e).[14,15] Four polystyrene model latexes, C428, PS3, PS4, and PS5, were used to assess the effect of M_w. Their particle sizes are close, as can be seen in Figure 5. However, their M_w differed because different amounts of chain transfer *tert*-dodecyl mercaptan (TDM) were added during synthesis. The molecular weights measured by GPC are listed in Table 3. The entanglement molecular weight (M_e) of polystyrene is around 13 300 g/mol.[16] The M_w of model latexes PS4 and PS5 is much less than twice that; that of PS3 and C428 is much higher than twice M_e. Figure 5 shows the freeze-fracture cryo-SEM images of the four suspensions. Pullouts are plainly evident when the particles' M_w exceeds twice M_e, as shown in Figure 5a and b. But when their M_w is lower than twice M_e, pullouts are no longer seen, for the fracture cleanly sliced through the particles, as shown in Figure 5c and d. Figure 6 puts forward the likely hypothesis for this difference. When M_w is higher than twice M_e, the polymer chains are entangled, and chain scission, which can produce brittle fracture, competes with disentanglement and disengagement, which contribute plastic yielding during fracture. Presumably, the disentangling chains align and associate into elongating stems (as in microfibrils of ordinary and thin film crazing) until they finally break. When M_w is lower than twice M_e, there evidently is little chance that polymer chains are entangled; consequently, the friction forces between chains are much smaller and they are more easily disengaged during fracture, leaving a cleanly sliced particle.

Effect of Cross-linking Density on Pullouts. Cross-linking of the latex particles' polymer surely raises tensile yield stress and depresses impact strength.[17] The cross-linked chains that span the incipient fracture must break rather than disentangle and disengage as the crack widens. Figure 7 shows cryo-SEM images of suspensions of reference model latex C428 and cross-linked model latexes C429, C430, and F157, all of whose mean particle sizes are close. However, they differ in cross-linking density of the polymer because increasing amounts of cross-linking agent butanediol diacrylate (BDDA) were added during synthesis. Pullouts are evident in Figure 7a, b, and c, but not in Figure 7d, which is an image of the latex that has the highest cross-linking density. Thus it seems that a critical value of cross-linking density ($D_{c,critical}$), below which a fracture can induce pullouts in frozen suspensions of polystyrene latex particles, corresponds to a concentration of BDDA that is between 5 and 15 wt %. Apparently, below the $D_{c,critical}$, enough of the polymer chains are not cross-linked and so remain sufficiently flexible and free to reptate that they can disentangle and align into a stem (and into ligament-like features on stem surfaces) as the crack opens and thereby form pullouts. Presumably any lightly cross-linked polymer chains can still be aligned and drawn until they break, which puts a greater load on the extending uncross-linked chains so that the pullouts break at shorter extension, as suggested by comparison of parts c and b of Figure 7. Figure 8 illustrates this hypothesis. But if the cross-linking density exceeds $D_{c,critical}$, the three-dimensional network of covalent bonding makes the latex particles so tough that the fracture goes around the particles and propagates through adjacent ice, as diagramed in Figure 8. The magnitude of $D_{c,critical}$ evidently

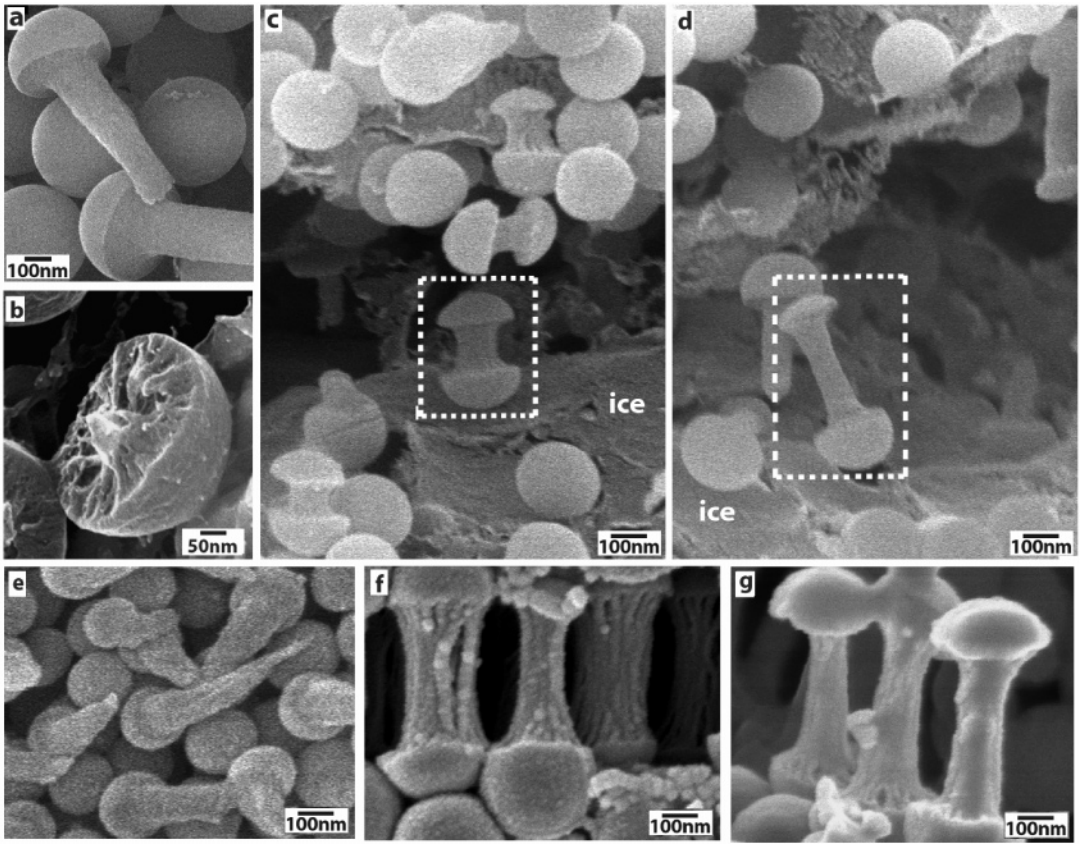

Figure 4. Cryo-SEM images of plastically drawn particles from frozen suspensions: (a) polystyrene latex with diameter 500 nm (courtesy of Dr. Y. Ma);[9] (b) an acrylic latex particle (courtesy of Dr. E. Sutanto);[9] (c) and (d) polystyrene particles in cracks of a 5 wt % suspension of F158 latex (unsublimated ice is visible); (e) reference polystyrene latex C428; (f) and (g) cryo-SEM images of plastically drawn poly(styrene-*co*-butyl acrylate) latex particles from freeze-dried suspension (courtesy of X. Gong).[12]

Table 2. Volume of Spool Compared with that of Its Original Sphere

rivets	average *r* of end caps (nm)	vol of sphere (10^6 nm^3)	vol of spool (10^6 nm^3)	vol of spool/vol of sphere
in Figure 4c	104.01	4.71	4.99	1.06
in Figure 4d	105.20	4.87	5.92	1.21

Table 3. Molecular Weight and Molecular Weight Distribution of Model Polystyrene Latexes C428, PS3, PS4, and PS5

model latexes	C428	PS3	PS4	PS5
M_w, g/mol	384177	63223	17482	7358
M_n, g/mol	156648	34785	9073	3797
M_w/M_n	2.45	1.82	1.93	1.94

depends on the polymer composition (cf., van Melick et al.[18]), the particle size, and the strength of particle−ice adhesion; other factors may be involved, too.

Effect of Nominal T_g on Pullouts. The micrographs in Figure 9 show pullouts on the freeze-fracture surface of particles of the reference model latex and two others that have different bulk polymer T_g's. The particle diameter in all three is about 130 nm, and the molecular weight is substantially greater than twice the entanglement molecular weight. The T_g of bulk polystyrene is 100 °C, of bulk poly(butyl acrylate), −54 °C.[10] That of bulk F193 poly(styrene-*co*-butyl acrylate) latex, as estimated with the Fox equation,[19] is about 3 °C. All three fracture surfaces were sublimated for 14 min; nevertheless, some ice remained between many pairs of the F194 particles that can be seen in Figure 9c. Because temperature as well as time of sublimation was well controlled, the reason is not clear (the image of a replicate sample looked the same). In the range of compositions examined, the results seem to show that the T_g of the bulk polymer does not affect the formation of pullouts.

Effect of Particle Size on Pullouts. Pullouts were seen in all our experiments, many not reported here, with suspensions of polystyrene latex particles ranging in diameter from 500 nm down to 30 nm. However, Disanayaka et al.[6] noticed in FFTEM images of poly(methyl-methacrylate) (PMMA) latex spheres that fractures produced pullouts from some particles 586 nm in diameter but none from larger ones 1250 and 1350 nm in diameter. The fracture plane passed almost exclusively through the center of the latter.

Challenges to Macromolecular Science

Glassy bulk polymer can deform plastically in two ways, depending on the fracture temperature and local strain rate: ductile shear deformation, or plastic yielding, and quasibrittle crazing, or nucleation of voids and development of ligments.[14,15] Neither way appears to relate to the brittle-to-ductile transition in compression of brittle solids as their particle size falls (cf., Kendall[20]). There is abundant evidence that molecular organization within submicron polymer particles synthesized by emulsion polymerization, especially at temperatures below the nominal T_g, differs from that in bulk.[21−23] We judge the hypothesis reasonable that the difference can greatly lower the yield strength, and likewise the elastic modulus, of which yield strength is ordinarily a fraction. However, there seem to be no measurements of single-particle Young's modulus, or shear modulus, and yield strength. Greatly lowered yield strength facilitates postyield plastic drawing. Indeed, van Melick et al.[24] reviewed evidence of toughness enhancement in polymer films as thin as 30 nm and in ligaments of comparable diameter.

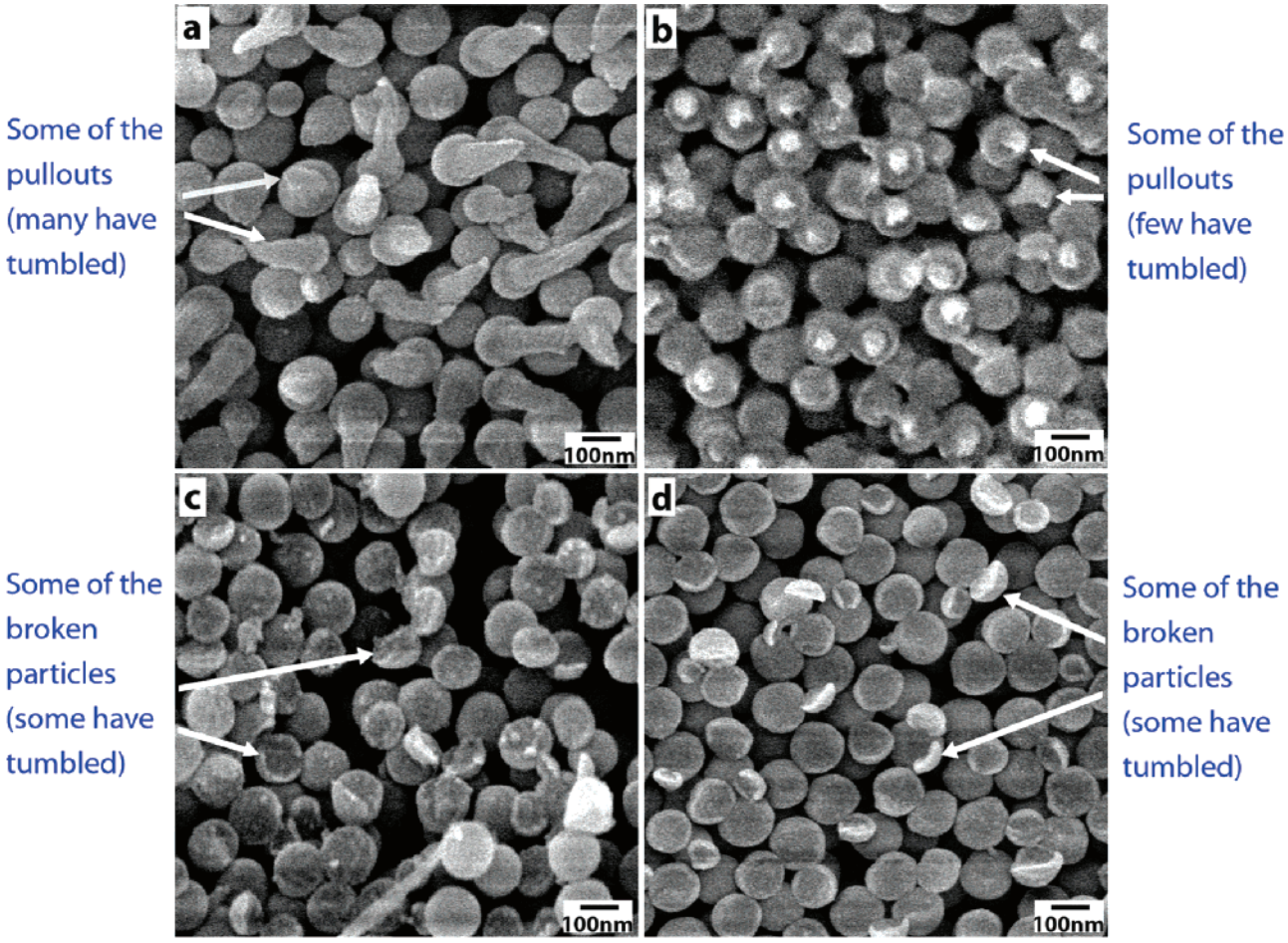

Figure 5. Cryo-SEM images of polystyrene latex suspensions of latex particles with different molecular weights: (a) M_w = 384 177 g/mol; (b) M_w = 63 223 g/mol; (c) M_w = 17 482 g/mol; (d) M_w = 7358 g/mol. The nominal entanglement molecular weight (M_e) of all is 13 300 g/mol.[16]

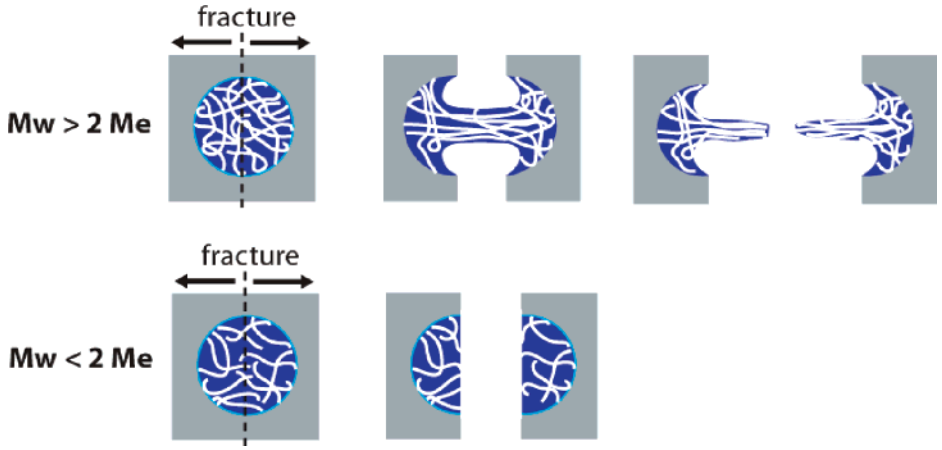

Figure 6. Hypothesized dependence of pullout formation on molecular weight M_w vs entanglement molecular weight M_e of the particle's polymer.

Notable is the report of van der Sanden et al.[25] that films of polystyrene less than 1 μm thick, sandwiched between layers of very weakly adhering polyethylene by a coextrusion process, readily deform plastically at room temperature, which is 80 °C lower than T_g of bulk polystyrene. Particularly relevant are the studies of craze microfibrils in polystyrene films less than 1 μm thick by Kramer and co-workers.[13,26]

On such films, they found plastically formed, fine surface grooves ahead of craze tips and transverse to the tensile principal stress, where the mean normal stress, or hydrostatic pressure, would have turned negative but for the presence of the deformable free surface ("lack of plastic constraint").

The analog at the surface of a latex sphere suffering tensile prying by an advancing crack in surrounding ice would be a plastically nucleated dimple, likewise transverse to the tensile principal stress where the hydrostatic pressure would have turned negative but for deformable particle surface having pulled free of the ice. As the tensile loading by the widening ice crack rose, it would be concentrated at the circumferential ends of the dimple, causing it to extend rapidly into a furrow. As the ice crack widened, the loading would continue to concentrate at the furrow's ends so that they propagate around to the particle's backside and girdle it. Meanwhile, the furrow would widen in the now-identifiable axial direction simultaneously with

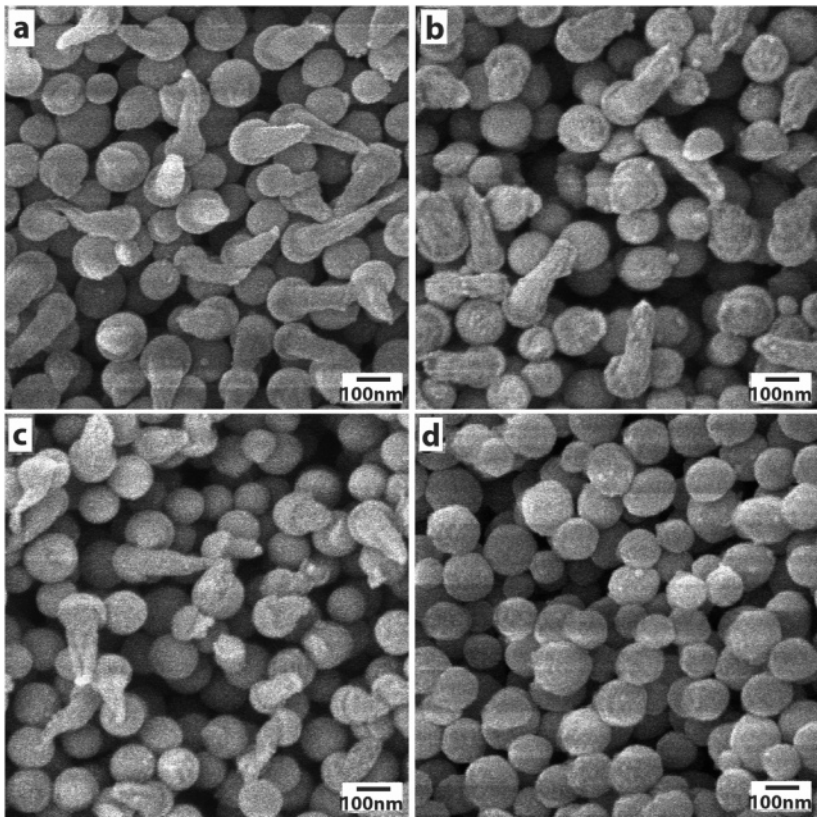

Figure 7. Cryo-SEM images of polystyrene latex suspensions of particles with different cross-linking density in particles: (a) no cross-linker; (b) 0.5 wt % cross-linker; (c) 5 wt % cross-linker; (d) 15 wt % cross-linker.

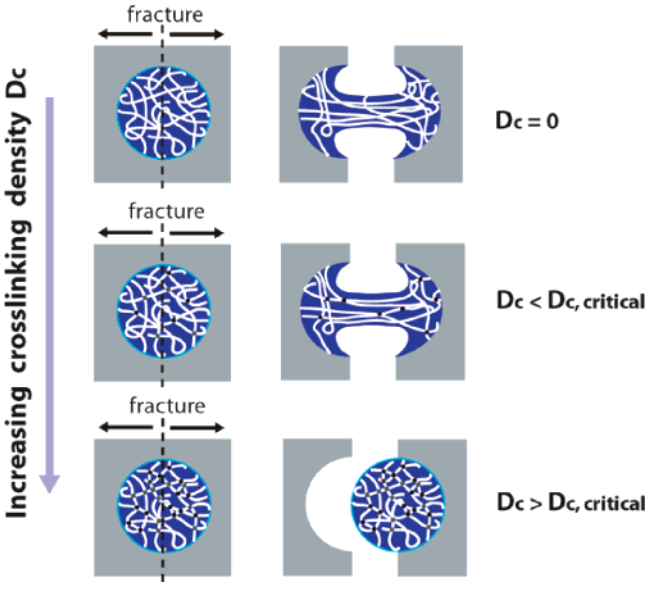

Figure 8. Hypothesized dependence of pullout formation on the cross-linking density D_c of polymer chains in latex particles. Experiments indicate a critical density for pullout formation.

the drawing of the polymer in the developing stem. The yielded and drawn material would surely be strain-hardened by extension, and by continuity, it would have to retract rapidly to become the surface layer of the developing furrow, which defines the lengthening shaft, or neck, or spindle. And if the yielding that produced the encircling furrow and accompanying radial retraction of material were not quite uniform, the nonuniformity could become amplified into the striations, ligament-like, and nanocraze-like textures of some of the shafts and annular surfaces in the micrographs. This analogy would account for the scenarios in Figures 2 and 3.

In this view, there is neither need nor circumstances for the cavitation that precedes crazing in bulk, or the perforation that precedes crazing in thin film; moreover, the geometry is distinctive from that of the latter. The process envisioned is a free-surface equivalent of crazing that could be called "furrowing". Like the grooving of thin films, its initiation is by incipient negative hydrostatic pressure at and near an existing free surface with gas or liquid, rather than by cavitation to create new free surface in a solid, or perforation to do that in a thin film. Its initiation by dimpling may be peculiar to the highly convex surface of submicron isometric particles, yet "furrowing" might also occur around narrow cylinders.

As for the yielding properties of polymer particles that develop pullouts, the strongest disturber of molecular configuration and entanglement is the confinement of the polymer chains from the time they grew from monomer within a spherelike volume no more than a fewfold larger in diameter than the radius of gyration of the polymer molecules in bulk material. SANS results indicate that coils are distorted from their equilibrium configurations in bulk and that the chains near the particle surface are perhaps preferentially oriented parallel to it. The consequent excess free energy may be the "driving force" responsible for more rapid interdiffusion of polymer between coalescing particles than across bulk interfaces. Particularly in particles polymerized below the nominal T_g, entanglements are likely to have been formed by the growth of "kinetic chains" of "reaction−diffusion" and to have been prevented from equilibrating in number or disposition.[27] Termination reactions are more likely to have occurred in the outer portion of the particles and lower-molecular-weight chains to have accumulated there;[27] both phenomena would contribute to radial variations in molecular configuration and entanglment.[20] Indeed, several research groups have measured the polymer glass transition temperature near the surface of a thin free-standing

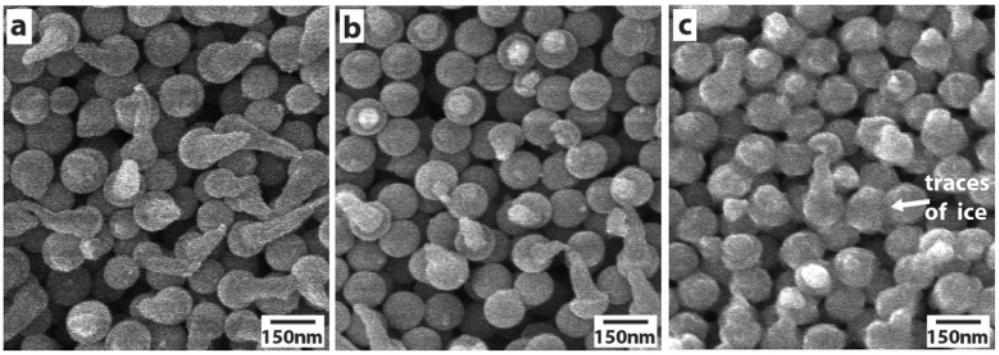

Figure 9. Cryo-SEM images of latex suspensions of polymer with different T_g: (a) reference polystyrene latex C428; (b) poly(styrene-*co*-butyl acrylate) model latex F193; (c) poly(butyl acrylate) model latex F194.

polymer film and have reported it to be lower than that of the corresponding bulk polymer.[28] Zhang et al.[29] found that the T_g of the zone within 20 nm of the surface of a polystyrene film could be 15 °C lower than that in the bulk. Presumably, the T_g of the surface zone of latex particles is likewise lower than that of bulk polymer because the molecular organization there differs in configuration and entanglement distributions. Forrest and Mattsson[30] used Brillouin light scattering to infer that the T_g of free-standing polystyrene film thinner than 30 nm is around 80 °C lower than that of bulk polymer.

What is remarkable is that pullouts form in particles as small as 30 nm in diameter. We conjecture that particles large enough that their interior organization is bulklike in molecular configuration and entanglement distributions are not susceptible to nucleation of furrowing by a crack tip arriving through ice, and so do not form pullouts but rather suffer brittle fracture or else adhesion failure and local delamination. Apart from the evidence of Disanayaka et al.,[6] it has not been possible to test the behavior of larger particles yet.

Summary

As a fracture approaches a particle, the stress field that accompanies it puts the adhesive contact between ice and polymer under tensile and shear stress. If the ice does not adhere strongly enough, the concentrated stress evidently initiates delamination in the particle−ice interface and the crack propagates along that interface and around one side of the particle; the particle remains lodged in the other fracture surface. Conversely, if the ice does adhere strongly enough, the concentrated stress must act on the disturbed polymer structure in the particle's surface zone. That action evidently either initiates a brittle fracture that cleanly slices a particle deficient in entanglements, or it initiates plastic yielding and necking of a particle that contains enough entanglements. In this view, the molecular weight of the polymer versus its entanglement molecular weight is crucial not only to the extension-to-break in the pullouts but also to the occurrence of pullouts at all. There may be appreciable static stress on the ice−polymer interfaces owing to differential volume change of polymer and water−ice during the fast-freezing process, which can be estimated.[31] How important this preexisting stress is to the competition between pluckout and fracture or pullout cannot yet be estimated because the adhesion strength between polystyrene particles and ice, without and with surfactant like sodium dodecyl sulfate adsorbed in the interface between them, seems not to have been measured (water-soluble oligomers, highly polar compared with polystyrene, may also concentrate in this interface).

The morphology of grossly deformed particles in fracture surfaces of frozen latex suspensions and, especially, in arrested side fractures, indicates a type of plastic yielding that is here pictured as furrowing, a highly curved free surface's rough equivalent of crazing, more closely related to free-surface grooving of thin polymer films.[13,26] This behavior at temperatures near 300 °C below the bulk T_g surely reflects the effects of confinement on chain conformations and alignment during polymerization and after, for which there is considerable other evidence. The morphology of grossly deformed particles further suggests a difference in yielding behavior between the particle's surface zone, which seems to give way more readily, and its core, which seems to strain-harden as it is drawn into pullouts of characteristic mushroom shape, spool shape, or awl shape. Pullouts have been seen in all suspensions examined of polystyrene latex particles of diameters from as low as 30 nm up to 500 nm. By analogy with the PMMA latex particles examined by Disanayaka et al.,[6] it appears that size becomes an important factor in large enough particles; further experiments are needed.

From the evidence, it appears that whether pullouts form depends on how near the midriff of a particle the advancing crack tip arrives and then on the outcome of a competition. The competition is between the strength with which particles adhere to the ice in which they are frozen and the force necessary to draw them until they neck and break to end up mushroom shaped or neck and detach to end up awl shaped. However, data about adhesion strength, yield strength, and postyield moduli are lacking.

In the model latex systems examined, pullouts form when the molecular weight (M_w) of the polymer chains in the particles is higher than twice the entanglement molecular weight (M_e). When M_w is less than twice M_e, latex particles are cleanly sliced through rather than plastically deformed. At least when M_w is greater than twice M_e, T_g does not affect the formation of pullouts. Cross-linking density greater than a critical value suppresses the formation of pullouts so that the particles are plucked out of one or the other fracture surface.

Pullouts effectively demonstrate that polymer mechanical properties in submicron particles synthesized by emulsion polymerization differ from those of polymer in bulk and in thin films, a matter warranting further investigation. Another matter, described elsewhere, is that after particles come in contact with one another in the consolidated (packed) stage, the compacting (deforming) stage, and the coalescing (film-forming) stage during drying of thin layers of suspension on a substrate, the morphology of the pullouts proves to be a useful indicator of the degree of interdiffusion of particles.[9,11,32]

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