

Electronic supplementary information

A. Ternary diagrams in oil/water/surfactant systems

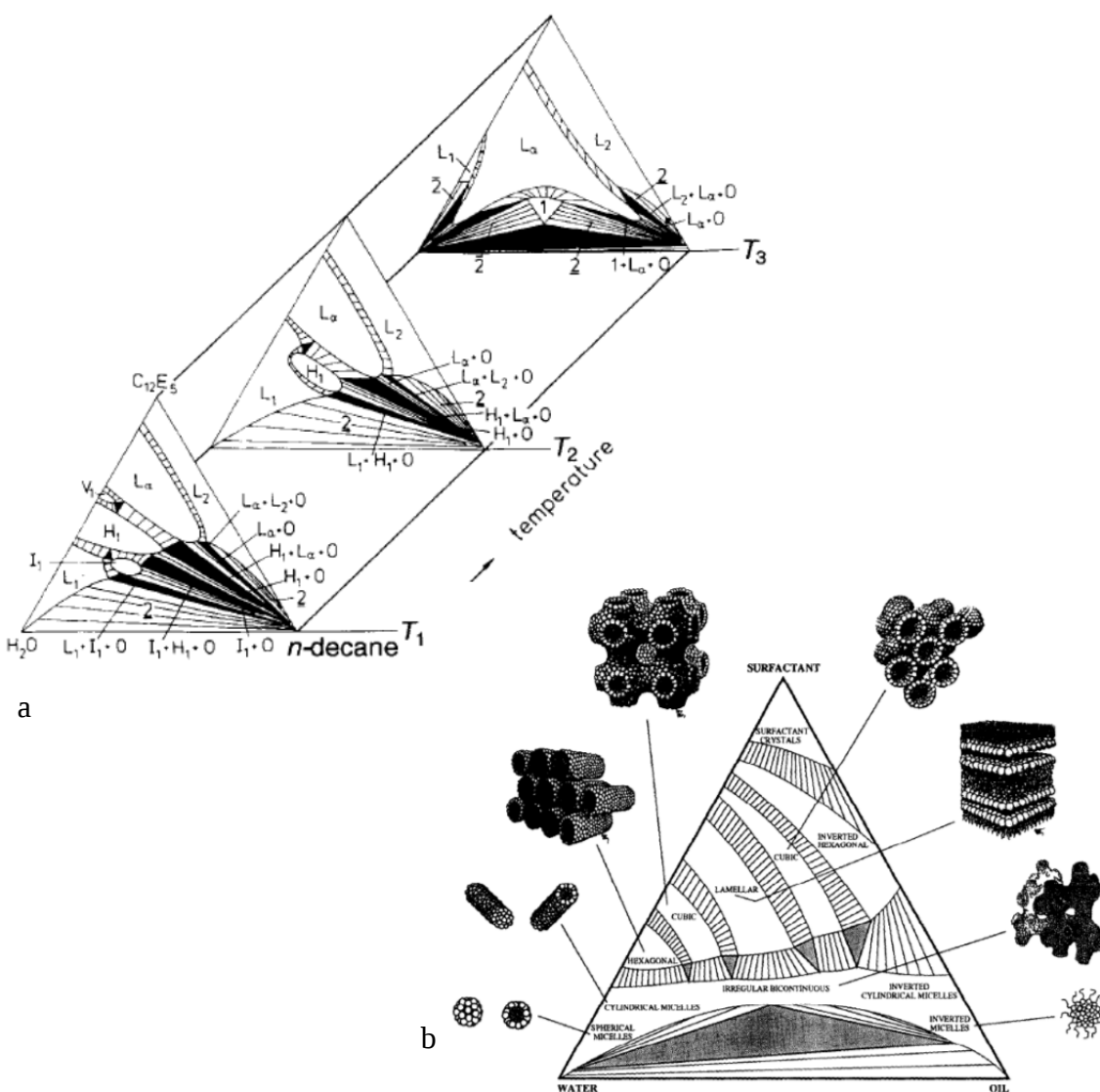


Fig. S1: (a) A ternary prism for decane/water/non-ionic surfactant mixtures showing changes in the equilibrium phase behavior as temperature is varied(1). Reproduced from Ref. (1) Leaver et al (1995) Phase-behavior and structure in a nonionic surfactant-oil-water mixture. *Journal of the Chemical Society-Faraday Transactions* 91:4269, with permission from The Royal Society of Chemistry. (b) Schematic of an equilibrium phase diagram of an oil/water/surfactant system showing the structures appearing in various regions(2). Reprinted from Ref. (2) Davis (1994) Factors determining emulsion type: Hydrophile—lipophile balance and beyond. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 91:9, Copyright (1994), with permission from Elsevier.

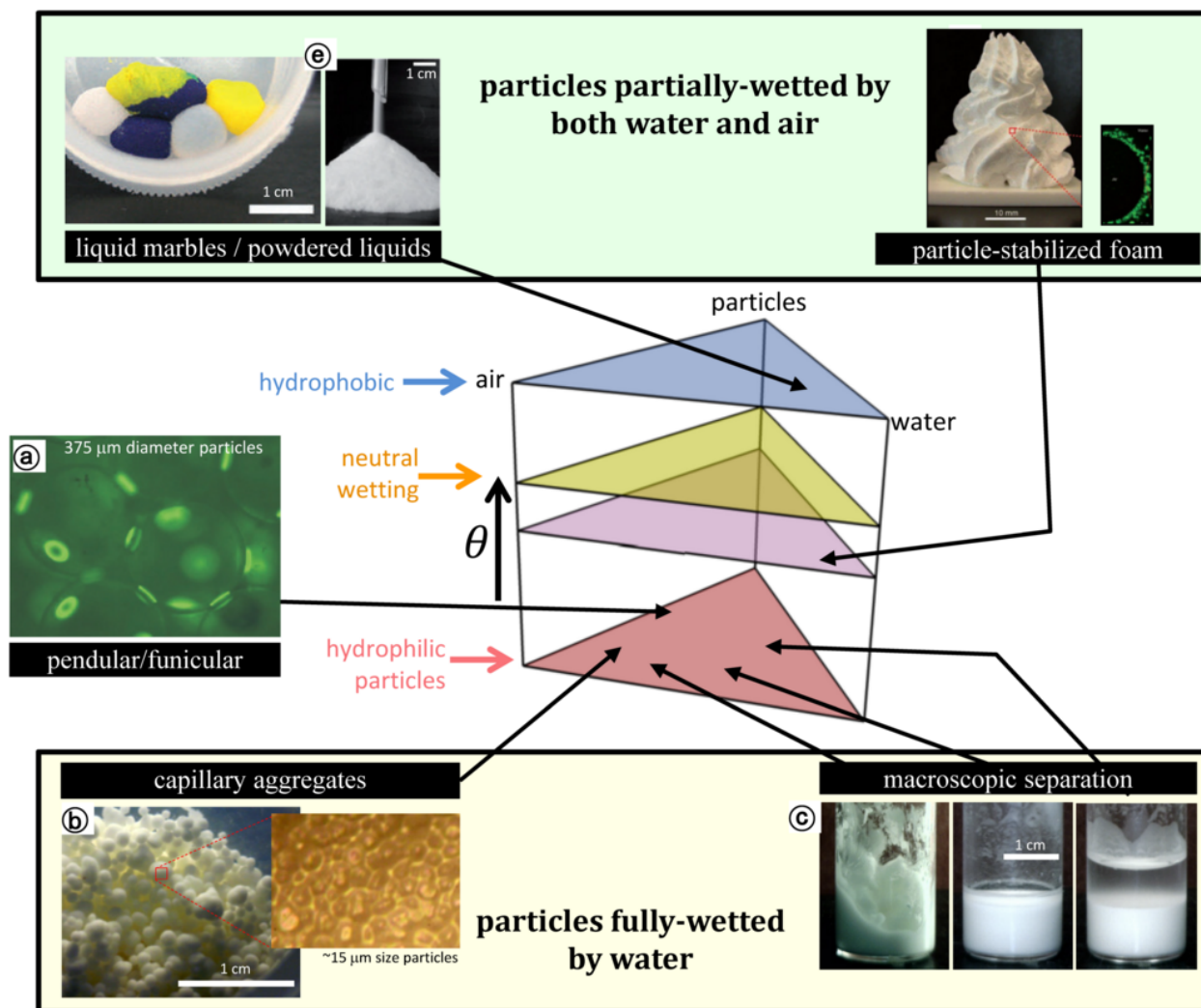


Fig. S2: Morphologies in various regions of the state prisms for water/air/particle mixtures. **(a)** pendular morphology(3), **(b)** spherical agglomerate; inset shows optical microscopy image of the surface with particles protruding outside (Velankar, unpublished), **(c)** particulate suspensions without entrained air bubbles (Velankar, unpublished). The leftmost image is a pasty particle-water mixture; the middle image is a concentrated suspension, the rightmost is dilute in particles and the particles have sedimented, **(d)** particle-stabilized foam(4) ; inset shows a confocal image of a foam bubble with particles at the interface, **(e)** liquid marbles and powdered liquid(5). **(a)** Reprinted from Herminghaus, *Advances in Physics*, 2005, **54**, 221(3) by permission of the publisher (Taylor & Francis Ltd). **(d)** Reproduced from Gonzenbach et al, *Angew. Chem.*, 2006, **45**, 3526(4) with permission from Wiley. **(e)** Reprinted by permission from Macmillan Publishers Ltd. from Binks and Murakami, *Nat. Mater.*, 2006, **5**, 865 (5); copyright (2006).

B. Experimental results of structural transitions in the ternary prism

This section will cite examples of structural transitions in ternary liquid/fluid/particle systems as the composition or wettability is changed. The literature on such ternary systems is vast, for example, with over a thousand papers on “Pickering emulsions” and over two thousand on “filled polymer blends”. The goal of this Supplement is to highlight exemplary cases from this literature in which structural transitions are noted as the composition or wettability is changed systematically. Each figure in this section has three parts: (1) a table with some details of the system, (2) images of the structure along a specific trajectory within the triangular prism, and (3) a triangle or triangular prism illustrating the corresponding trajectory as a red line. In some cases, the original articles also examined structural changes along other trajectories in the composition diagram, and these are shown as dotted black lines.

The first section B.1 below concerns situations where the particles are fully-wetted by one phase, and in these tables, the phase that fully-wets the particles is dubbed “B” whereas fluid “A” is regarded as non-wetting. Section B.2 concerns situations where the particles are partially-wetted by both phase. Here the phase that preferentially-wets the particles is generally dubbed B, although in some cases, the illustrated trajectory traverses a range of wettabilities.

B.1 Fully-wettable systems

Fig. S3(6) and S4(7, 8) both correspond to adding increasing amounts of fully-wetting fluid to a particulate system. Fig. S2 shows cross sections (obtained by x-ray tomography) of a bed of wet granular particles with ~58 vol% particle loading, and air as the continuous phase. A small amount of water was added, mixed by fluidization, and followed by a long rest time. During the rest time, the water is presumed to have equilibrated throughout the sample. Fig. S3 shows that at low water content, the water is present as pair-wise *pendular bridges* between the particles. With increasing water fraction, the menisci grow and coalesce, and may eventually encapsulate some of the particles.

Fig. S4 shows mixtures of particles and two immiscible polymers prepared by melt blending. The particle size is roughly 100-fold smaller, and the viscosity is at least 10^4 times higher, as compared to Fig. S4. The particle loading is 10 vol%. Due the small particle size and high viscosity, the particles do not sediment significantly prior to quenching the sample, and hence the structure obtained by *ex situ* electron microscopy is well-representative of the structure immediately after mixing. Despite the difference in particle size, fluid viscosity, and particle loading as compared to Fig. S3, the structures observed are similar. Once again, a pendular structure is evident when the wetting fluid is dilute. With increasing wetting fluid loading, menisci first coalesce into *funicular clusters*. Upon raising the wetting fluid content

even higher, (typically to 25-80% of the particle loading), the particles are completely engulfed into capillary aggregates. Similar pendular menisci have been seen by confocal imaging in systems where the two liquids are oil and water (Koos et al. personal communication). Pendular and funicular aggregates appear even the preparation method is completely different, e.g. quenching a liquid-liquid mixture from a single phase to a two-phase state in a particle bed(9), or allowing gravitational drainage through a packing of particles(10, 11).

Fig. S5(12) shows the same pendular and capillary aggregate states in an oil/water/hydrophilic particles system, but then also shows higher wetting fluid (water) content. In this case, the samples were prepared by simply shaking the components in a vial. Pendular aggregates were reported at the lowest particle loading by optical microscopy (not reproduced here). Upon increasing the wetting fluid loading, capillary aggregates are visible as small compact lumps at the bottom of the vial. Upon increasing the water content slightly beyond that needed for capillary aggregates, the mixture rapidly undergoes macroscopic phase separation into an oil layer resting on a large “blob” of the particle-in-water aqueous phase. The same sequence of transitions, from pendular aggregates to capillary aggregates, to macroscopic separation were shown by Sirianni et al(13) in oil/water/hydrophobic particle systems and by Domenech and Velankar(12) in polymeric systems. Liquid/air/particle systems also show the same sequence of transitions (discussed below). As mentioned in the main article, industrial processes variously known as *wet granulation*, *spherical agglomeration*, or *oil agglomeration* all rely on capillary aggregate formation, and substantial literature in that context(14-19) shows the same sequence of transitions.

Fig. S6 shows the effect of adding particles while holding the fluid volume ratio fixed. This system is similar to that in Fig. S4, except that the particles are an order of magnitude larger and the fluids are an order of magnitude less viscous; accordingly gravitational effects are much stronger in Fig. S6. Yet, similar to Fig. S4, since the drops can be frozen by cooling, the structure can be quenched in a fashion not possible with oil/water systems. The particle-free system has the wetting fluid (which is in a minority) as the dispersed phase. Addition of a small amount of particles is seen to increase the drop size, an effect also seen previously in other systems(20-22). With further addition of particles, the system progresses from a particles-in-drop structure to very poor mixing, i.e. macrophase separation. Thus, macroscopic phase separation appears to be a common feature of ternary systems if the particle volume fraction is comparable to the wetting fluid fraction. The reasons for this are discussed in the main text.

Upon further increase in the wetting fluid, phase inversion is expected so that B becomes the continuous phase. Studies of the effect of fully-wetting particles on phase inversion are uncommon in the literature. Fig. S5(12) illustrates an example of phase inversion in an oil/water/hydrophilic particle system as the

water:oil ratio is increased at fixed particle loading. Phase inversion was seen to proceed gradually where, starting from the completely separated state, an increasing amount of the oil is incorporated into the aqueous phase fluid until no free oil remained. It must be emphasized that in such low viscosity systems, gravity rapidly induces sedimentation and then coalescence. Thus observations such as Fig. S5 correspond to post-mixing conditions. In polymeric systems with much higher viscosity, as mentioned above, sedimentation is negligible, and hence the structure during mixing conditions can be quenched easily. Fig. S7 shows such an example(23). Here the particles were pre-dispersed into the fully-wetting phase (polymethyl methacrylate), and then this combined phase was melt-blended with polystyrene at various ratios. Similar to Fig. S5, in such a case as well, that phase inversion proceeds continuously: as the volume of one phase increases, it entrains increasing amounts of the other in the form of drops. Some of the morphologies in Fig. S7 appear bicontinuous, which is common in polymer systems. This article(23) did not report on blends with highly mismatched fluid volume ratios, but we presume that if either phase was in a small minority, it would form a more conventional droplet-matrix structure.

Fig. S8(24) shows that phase inversion can also be induced by increasing the particle loading at fixed fluid volume ratio. The system is seen to move from a particles-in-drops structure to a drops-in-suspension structure. This specific example was not realized by mixing, but instead by phase separation: the two polymers were partially-miscible with a upper-critical solution temperature. The ternary mixtures were first held at high temperature at which the two polymer liquids formed a single homogeneous phase. Cooling into the two-phase region induced phase-separation. Another unusual aspect of this experiment is that it is a 2D experiment: the sample thickness was comparable to a single particle diameter. Thus, Fig. S8 is somewhat different from most of the other examples in this paper. Nevertheless, recent experiments in our lab(25) confirm the main point of Fig. S8 that phase inversion can be induced by raising particle loading. This is not surprising: as explained in Section 4.2 in the main article, the particles and the wetting fluid form a combined phase. With increasing particle loading, this combined phase increases its volume fraction and tends to become the continuous phase.

In melt-blended polymeric systems, changes in phase continuity often include bicontinuous or fibrillar structures. Fig. S9(26) shows an example of adding various amounts of fumed silica to blends of polystyrene and polylactide (the latter is fully-wetting towards the particles). The particle-free blend has a droplet-matrix structure with the non-wetting phase (which is in a minority) becoming the dispersed phase. Addition of 5 wt% fumed silica induces a transformation into into a bicontinuous structure. Similar results were shown by Lee et al.(27) Sometimes addition of particles may convert a spherical dispersed phase into a highly irregular dispersed phase without reaching full continuity(28, 29). Another example from molten polymeric systems is provided by Fig. S10(30). Unlike Fig. S9, the non-wetting phase is in a

majority, and the initial the particle-free blend is bicontinuous (Fig. S10a). Addition of particles destroys the bicontinuity. At low particle loadings, the combined (particle+wetting fluid) phase takes the shape of rounded drops. At higher particle loadings, the combined phase forms elongated fibrils.

We briefly now comment on the similarities and differences when one of the fluids is air. One significant difference is that in a gravitational environment, the overall composition cannot be controlled exactly: only the liquid:particle ratio can be controlled. The materials and the mixing method then determine how much air gets incorporated into the structure. Nevertheless, at low liquid loadings, pendular structures are seen (Fig. S2a & Fig. S3), and these transition into funicular structures as the liquid loading increases(31). With further increase in wetting fluid, capillary aggregates are formed (Fig. S2b). Formation of capillary aggregates is the basis of *wet granulation*, a process used to increase the size of fine powders(15, 32). This process is analogous to the spherical agglomeration process mentioned above, except that wet granulation involves liquid/air/particle mixtures. The process consists of spraying a wetting liquid (in this context called a *binder*) onto a bed of particles, and mixing to induce the growth of strong and compact capillary aggregates. Finally, analogous to the liquid/liquid/particle cases above, liquid/air/particle mixtures also undergo macroscopic phase separation when the liquid volume is roughly equal to the particle volume. Indeed, in the context of wet granulation processes, it is well-recognized that excess binder can create a pasty liquid/particle mixture (leftmost image if Fig. 2c) which does not form compact aggregates(33). In a formal sense, this may be regarded as macroscopic separation of the air from the aqueous phase. Incidentally, a kitchen table experiment can readily demonstrate this entire sequence of transitions: shaking starch granules with a small quantity of water first gives a “moldable” material analogous to wet sand. Upon increasing the water content, capillary aggregates such as shown in Fig. S2b are formed. Adding even slightly more liquid gives a pasty particle-water mixture corresponding to macroscopic separation, followed by increasingly dilute suspensions in which particles may settle(Fig. S2c).

In summary, at small loadings of wetting fluid liquid/air/particle mixtures are completely analogous to liquid/liquid/particle mixtures, and show the same sequence of pendular-funicular-capillary-separated states. With further increase in wetting liquid however, the analogy breaks down: there is no analog to phase inversion when one of the fluids is air, at least not when particles are completely wetted by the liquid. Instead, when the liquid loading increases to a sufficiently high value, one usually obtains a suspension of particles in the liquid, rather than a phase-inverted foam. While some air may be entrained during mixing conditions, the bubbles rise rapidly under quiescent conditions, and the air is excluded completely from the liquid phase. A notable exception to this, polymer foams with filler particles in the polymer phase, was mentioned in the main text. Such foams are prepared by methods significantly more

complicated than simple mixing and aeration(34, 35). The particles and a *blowing agent*, i.e. something capable of releasing gas, are mixed into either a molten thermoplastic polymer (e.g. polystyrene foam) or a reacting monomeric liquid (e.g. polyurethane foam). Heating or chemical reaction releases gas from the blowing agent, bubbles are nucleated, and grow to form a foam. Finally the continuous phase liquid is quenched into a solid by cooling or crosslinking. Typical particle loadings in polymer foams are only a few volume percent(36-39), although occasional cases with few ten volume% particles have been reported(40). Although such polymer foams are formally ternary liquid/air/particle systems, their structure development is governed by physical phenomena (e.g. effect of particles on bubble nucleation, or polymerization reaction kinetics) rather different from those discussed in the rest of this paper.

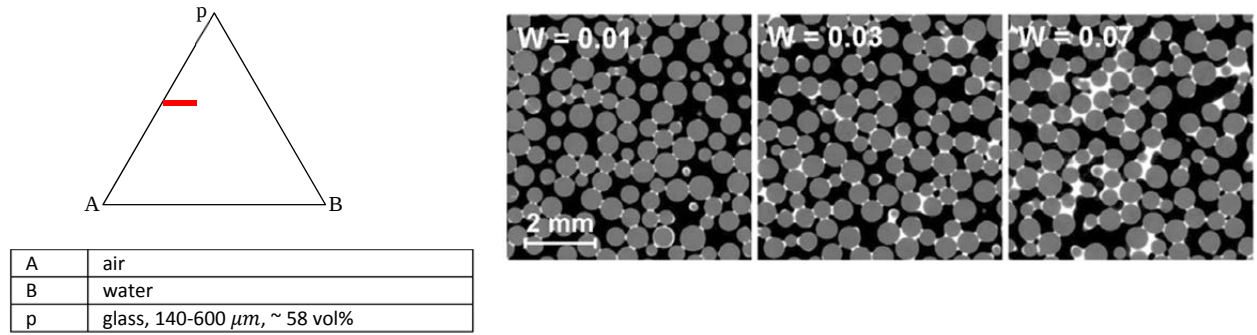


Fig. S3: Cross section of a bed of wet glass beads obtained by x-ray microtomography at three water contents. W is the defined as the volume of wetting liquid divided by the total volume the wet granulate, i.e. W is equivalent to ϕ_B as defined throughout this paper. Note the purely-pairwise nature of the menisci at $W=0.01$, and the significant coalescence of the menisci at $W=0.07$. Copyright IOP Publishing. Reproduced from Ref. (41), Scheel et al (2008) Liquid distribution and cohesion in wet granular assemblies beyond the capillary bridge regime. *J. Phys.: Condens. Matter* 20:494236 by permission of IOP Publishing. All rights reserved.

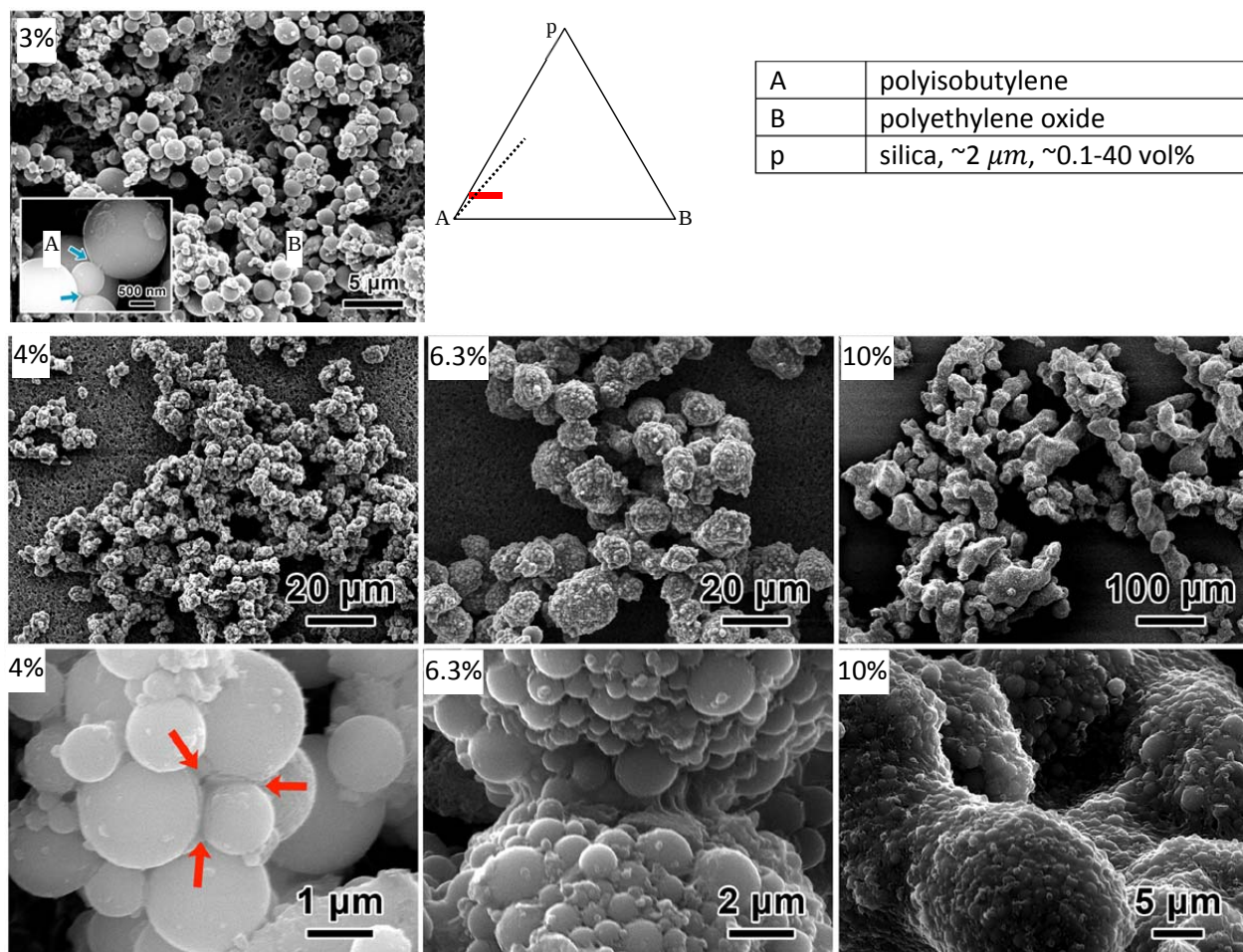


Fig. S4: Microstructure of blends of polyethylene oxide (PEO), polyisobutylene, and silica particles (10 vol%)(7). The PEO content is noted at the top left of each figure. The continuous phase polyisobutylene has been removed by selective dissolution. The bottommost row is a magnified view of the middle row. The inset in the top left figure shows a magnified image of the pair-wise meniscus (indicated by arrows) at 3% PEO, and similar structure was noted at even lower loadings. Note the partial coalescence of the capillary aggregates at 6.3% PEO. Note also the significant increase in the size of the dispersed phase going from 4% to 10% PEO. Top left image is reproduced from Ref. (7), Domenech & Velankar (2014) Capillary-driven percolating networks in ternary blends of immiscible polymers and silica particles. *Rheol. Acta* 53:1 with permission. Lower six figures are reproduced from Ref. (8), Domenech & Velankar (2015) On the rheology of pendular gels and morphological developments in paste-like ternary systems based on capillary attraction. *Soft matter* 11:1500, with permission from The Royal Society of Chemistry.

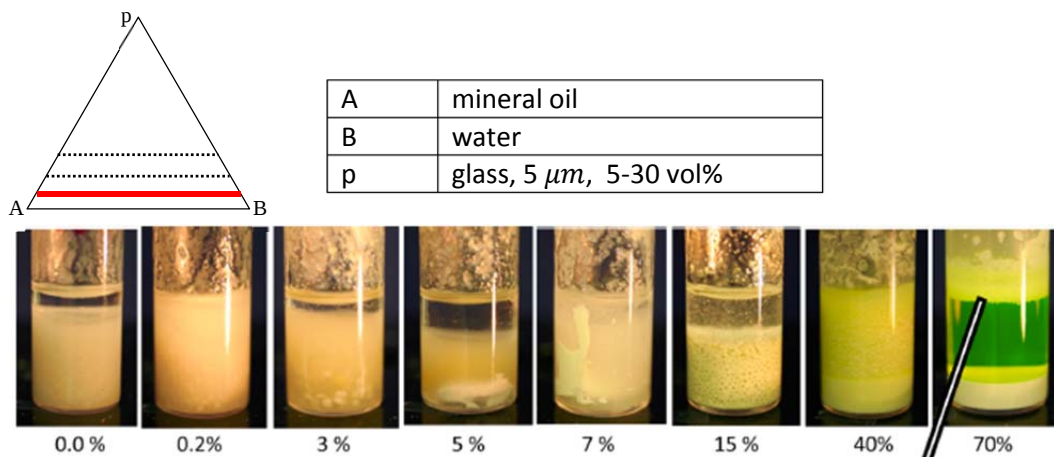


Fig. S5: Structure of oil/water/particle mixtures 20 wt% (roughly 10 vol%) particles. The number below each image is the weight % of water. The small white “lumps” at 3% water are capillary aggregates. The large white “blobs” of particles-in-water at 5% and 7% water are pasty sediments, which indicate near-complete separation of the oil and the aqueous phase. Note also the oil drops incorporated into the aqueous phase at 15% water. These indicate gradual phase inversion: with increasing amounts of water, increasing amounts of oil become trapped in the aqueous phase. Reprinted with permission from Ref. (12), Heidlebaugh et al (2014) Aggregation and Separation in Ternary Particle/Oil/Water Systems with Fully Wettable Particles. *Langmuir* 30:63, Copyright (2014) American Chemical Society.

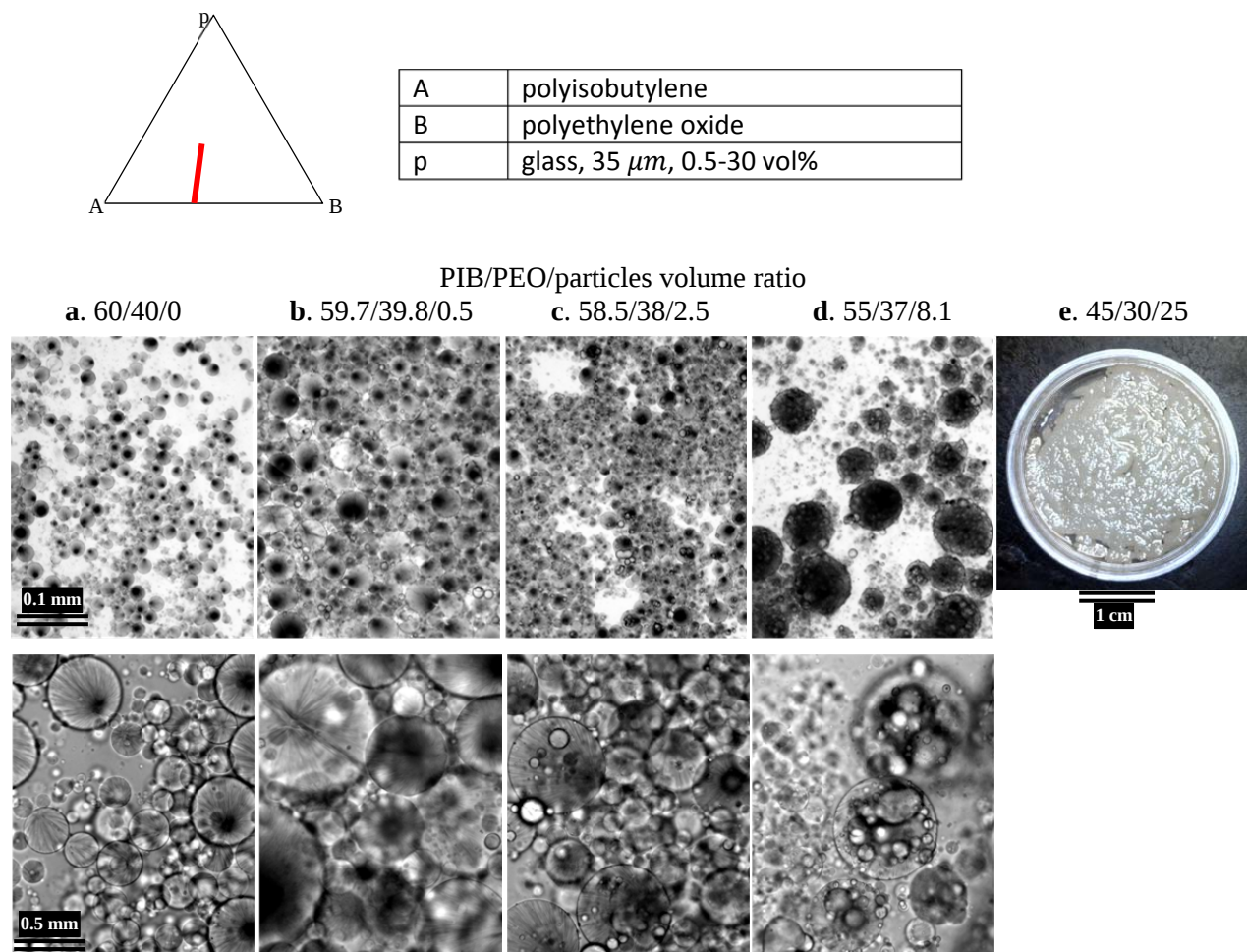


Fig. S6: Structure of blends of glass particles, polyisobutylene, and polyethylene oxide (PEO) as particles are added at fixed ratio of the two fluids. Images in bottom row are same as in the top row, but at higher magnification. The same scalebars apply to all images in the top row from a-d, and bottom row a-d. This system is similar to Fig. S3, but the particles are far larger and the fluids have a much lower viscosity. The mixtures were prepared under molten conditions and cooled to room temperature at which the PEO is crystalline. The “textured” appearance of the PEO drops is due to their crystallization into a spherulitic structure. Note the increase in drop size at very low particle loading (b) suggesting that particles promote coalescence. At 25 vol% particles, (e), the system cannot be mixed homogeneously even though the mixing conditions were identical to those for the remaining samples. Samples and images courtesy of Luke Brady, U. Pittsburgh.

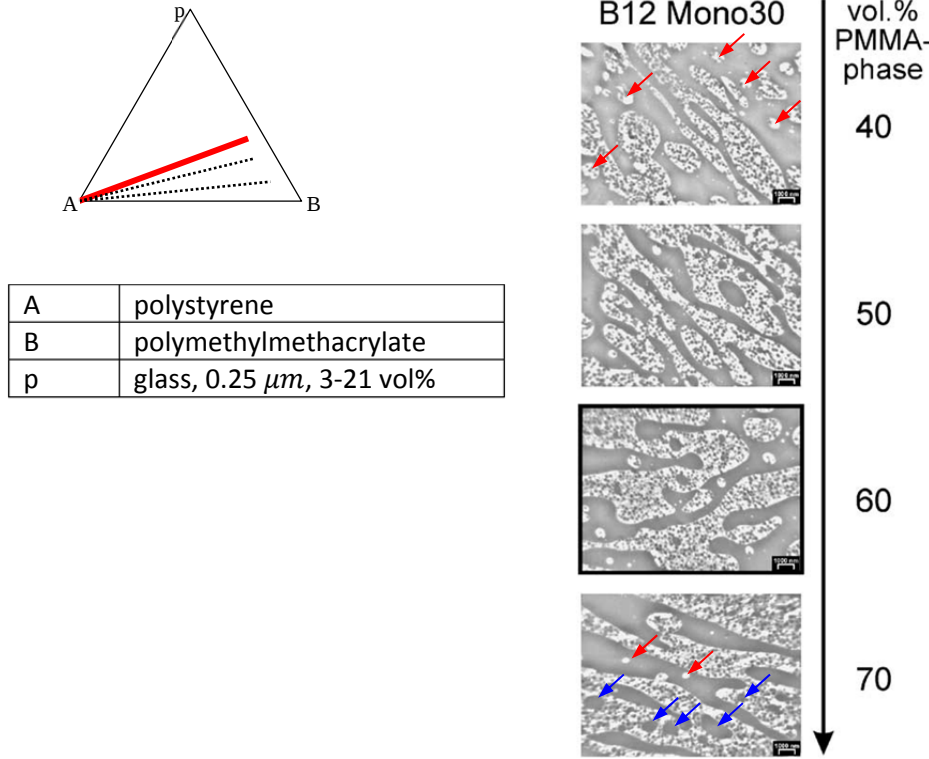


Fig. S7: Morphology of melt-blended samples of glass particles and two molten immiscible polymers. Lighter phase polymethylmethacrylate (PMMA) contains 30 vol% particles. The numbers far right are the volume % of the (particles + PMMA) combined phase, i.e. in the notation of this paper, $(\phi_B + \phi_p)$. The red arrows indicate (PMMA+particles) inclusions in the continuous phase polystyrene, whereas the blue arrows indicate polystyrene inclusions in the continuous phase (PMMA+particles). Note the gradual phase inversion : the topmost figure has only red arrows, whereas the bottommost figure has mostly blue arrows. Images reprinted from Ref. (23), Steinmann et al (2002) Influence of selective filling on rheological properties and phase inversion of two-phase polymer blends. *Polymer* 43:4467, Copyright (2002), with permission from Elsevier.

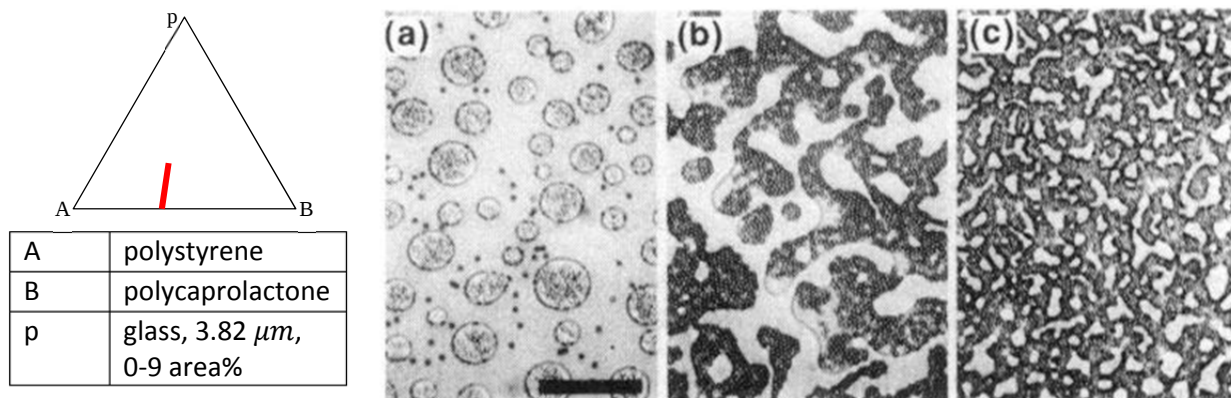


Fig. S8: Morphology of mixtures of glass particles and two partially-miscible molten polymers(24). The samples started as at high temperature where the two polymers were miscible and formed a single fluid phase. Quenching into the two-phase region induced phase separation into two liquid phases, with the polycaprolactone-rich phase wetting the particles completely. Note that these are effectively 2D experiments, i.e. sample thickness was comparable to the particle thickness. Note the change in phase continuity: the polystyrene is the continuous phase in (a), but the dispersed phase in (c). The scale bar is 100 μm . Figure reproduced with permission from Ref. (24), Tanaka et al (1994) Pattern Evolution Caused by Dynamic Coupling between Wetting and Phase-Separation in Binary-Liquid Mixture Containing Glass Particles. *Phys. Rev. Lett.* 72:2581, Copyrighted by the American Physical Society.

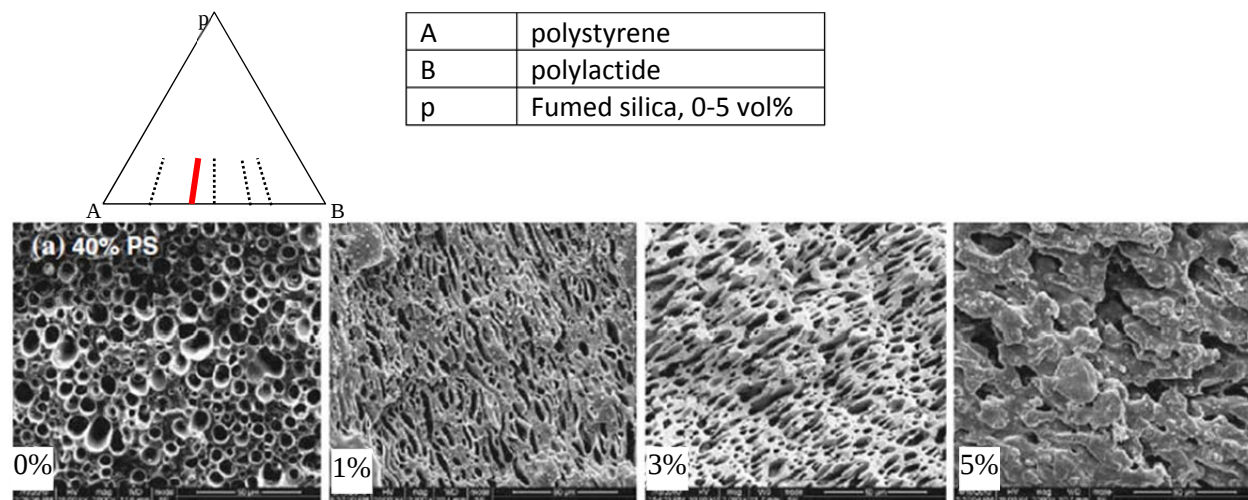


Fig. S9: Changes in phase continuity of melt-blended samples(26) as particle loading is increased keeping the polystyrene:polylactide ratio as 40:60. Particle loading is listed in vol% in the bottom left corner of each image. In each case, the polystyrene phase has been extracted in a selective solvent. Note that the polystyrene is the dispersed phase at 0% particles, but both phases are continuous at 3 and 5% particles. The scalebars at the bottom of each image are 50 μm . Figure reproduced from Ref. (26), Zhang, et al (2012) Morphology and rheology of poly(L-lactide)/polystyrene blends filled with silica nanoparticles. *J. Mater. Sci.* 47(3):1339, with kind permission from Springer Science and Business Media.

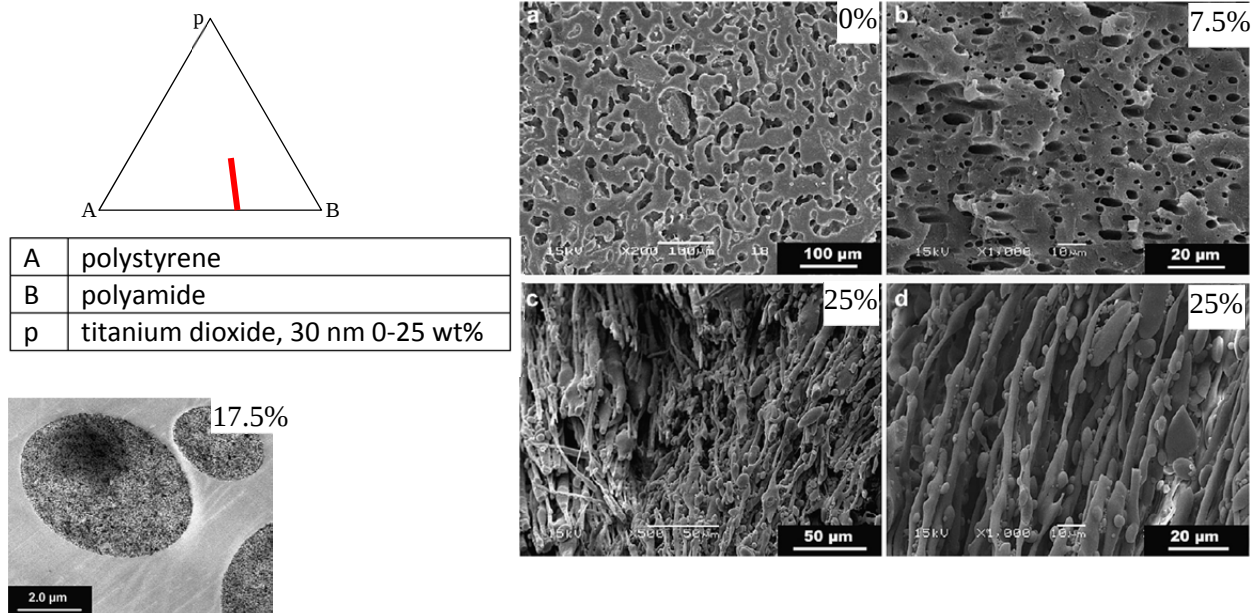


Fig. S10: Changes in phase continuity of melt-blended samples(30) with particle loading (listed in weight % at the top right corner of each image). The transmission electron microscope image bottom left shows the particles being engulfed by the polyamide phase. In (a) and (b), the polystyrene phase is visible (the polyamide phase has been removed by selective dissolution). In (c) and (d) (which are the same sample but at different magnification), the polyamide phase is visible (the polystyrene phase has been removed by selective dissolution. Samples (a-d) all have the same polystyrene:polyamide weight ratio of 70:30. Note the changes in phase continuity: at 0% particles, both phases are continuous; at 7% and 17.5% particles, the polystyrene phase is continuous and the polyamide is only slightly elongated; at 25% particles, the polystyrene phase is continuous and the polyamide phase is fibrillar. Images reprinted from Ref. (30), Cai et al (2012) Morphology evolution of immiscible polymer blends as directed by nanoparticle self-agglomeration. *Polymer* 53:259, Copyright (2012), with permission from Elsevier.

B.2 Partially-wettable systems

The region near the bottom edge of the triangle where particles are dilute as compared to both the liquid phases has been heavily studied in the oil/water/particle Pickering emulsion literature. In such Pickering emulsions, the partially-wetted particles cover the drops and stabilize the emulsion against coalescence – a role that, in conventional emulsions, is played by molecular surfactants(42, 43). An immediate question then is: which phase becomes the continuous phase of the emulsion? Even the very early literature on this topic recognized that the liquid that is preferentially-wetted by the particles becomes the continuous phase(44). Much of this literature has been reviewed by Tambe and Sharma(45). More recently, a comprehensive set of results supporting this have been obtained by Binks and Lumsdon. Fig. S11⁽⁴⁶⁾ shows an example where oil/water emulsions were prepared across a range of oil/water ratios, with the

particles being dilute. The relative wettability of the particles towards the two phases was varied *via* chemical modification of the surface of the particles. Fig. S11 shows that at equal volume of oil and water (horizontal line), the oil is the continuous phase when the particles are more hydrophobic, whereas water is the continuous phase when they are more hydrophilic. With increasing hydrophobicity, an increasing fraction of water is needed for water to become the continuous phase.

Changing the surface chemistry of the particles, as in Fig. S11, is not the only way to change the relative wettability of the particles towards the two phases. Another method is to change the oil phase while keeping the particles the same. Binks and Lumsdon(47) found that when the oil was relatively polar, it became the continuous phase, whereas when the oil had very low polarity, the water became the continuous phase. Contact angles measured against flat substrates of the same surface chemistry as the particles support the results as in Fig. S11: as the oils became progressively more wetting towards the particles (equivalent to the particles becoming more hydrophobic), the oil tended to become the continuous phase. Similar results have been shown by Read et al.(48)

Yet another approach to changing the relative wettability of the particles is to mix hydrophobic and hydrophilic particles to realize different mean wettabilities. In this case, Binks and Lumsdon(49) showed that with hydrophilic particles, only water became the continuous phase. As the fraction of hydrophobic particles increased, the emulsion inverted, and oil became the continuous phase.

The relative wettability of the particles towards the two liquids can also be tuned by adding surfactant. An exemplary case is shown in Fig. S12. Tambe and Sharma(50) measured oil/water contact angles on polished calcium carbonate crystals to show that calcium carbonate was preferentially-wetted by pure water, but it became progressively hydrophobic with addition of the surfactant stearic acid (Fig. S12a). Calcium carbonate particles were then used to prepare emulsions. The phase continuity of the emulsions (Fig. S12b) tracked changes in wettability: the emulsions had water as the continuous phase in absence of surfactant, but inverted to having oil as the continuous phase when sufficient surfactant was added. Similar inversion of the emulsion may also be effected by changing the wettability of particles due to other surfactants or changes in pH(48, 51-62).

Much of the above literature on Pickering emulsions was conducted with particles that were “non-ideal” in many respects, i.e. polydisperse, non-spherical, or even porous (e.g. fumed silica which is composed of ~15 nm silica particles fused together into porous, fractal-like aggregates). Yet, a very recent and beautiful study by Destribats et al.(63) has used extremely well-characterized spherical monodisperse particles of tunable wettability to obtain the same result: the liquid that is preferentially-wetted by the particles becomes the continuous phase of the emulsions. These results are shown in Fig. S13. What is

most noteworthy about this research is that the contact angles on the exact same system were measured by electron microscopy; to our knowledge, this is the only article that conclusively shows that phase inversion occurs when the contact angle is near 90° . Finally, Fig. S14(64) shows emulsions in the same region of composition space (dilute particles) but prepared by a completely different method. In this case, a homogeneous single-phase liquid was quenched into the two-phase region and allowed to phase-separate with no applied mixing flow. Despite the different preparation method, Fig. S14 yields the same result: shows that the continuous phase is the one that preferentially-wets the particles. Incidentally, Fig. S14 shows a bicontinuous structure to be discussed later. In summary, this result appears very consistent: the “favorable” emulsion is the one in which the preferentially-wetting fluid is the continuous phase, i.e. the particles prefer to protrude out of the drops rather than into the drops. The “unfavorable” emulsion can be prepared of course, for instance, Fig. S11 showed that by simply diluting the preferentially-wetting liquid sufficiently, it can be forced to become the dispersed phase. Such inversion induced by changing the relative volume of the phases is called *catastrophic inversion*.

The above discussion immediately raises the question of what happens if neither phase is preferentially-wetting, i.e. if the particles are equally-wetted by both phases. Perhaps the research that addresses this most directly is Destribats et al.(63): since they actually measured contact angles directly, conditions of equal wettability could be determined unambiguously. This article reported that a 90° contact angle gave poor emulsion stability (Fig. S13b), i.e. neither oil-in-water nor water-in-oil emulsions were stable when particles are equally-wetted by both phases. We may also look into studies of *transitional inversion*, i.e. phase inversion occurring at fixed volume ratio of the two liquids due to changes in temperature, pH, or addition of surfactant (e.g. Fig. S12). Most articles on transitional inversion of Pickering emulsions did not measure contact angles at all. In some cases(50, 65), contact angles were measured on a similar system, e.g. in Fig. S12 contact angles were measured on a flat surface of the same material as the particles. Yet, it is plausible that transitional phase inversion roughly corresponds to equal wetting by both phases, and therefore, emulsion stability near transitional phase inversion may be also be indicative of behavior near equal wettability. Such studies offer conflicting evidence. For instance, Fig. S12 shows that at intermediate wettability in the vicinity of phase inversion, the emulsion is unstable under quiescent conditions, and readily separates into two phases due to coalescence. Other papers have also reported unstable emulsions near transitional inversion when wettability was changed by varying the pH, or salt content(45) or surfactant(66). A much older article by Briggs(44) reported that hydrophilic and hydrophobic particles (which individually stabilized oil-in-water and water-in-oil emulsions respectively), when mixed, gave highly unstable emulsions. All these examples support the idea that particles with equal wettability towards both phases gives unstable emulsions. On the other hand, several papers reach

the exact opposite conclusion: they show that Pickering emulsions are highly stable near transitional inversion(48, 51-55, 58, 59, 62). These include a diversity of particle types: fumed silica, colloidal silica, latex, or clay. Finally formation of double emulsions i.e. emulsions with a drop-within-drop structure(55, 64, 67-69) has also been noted. In summary, the question of emulsion stability with equally-wettable particles remains unsettled; it is possible that the conflicting results may be due to factors other than particle wettability, e.g. the rheological characteristics of the interface.

We now turn to morphologies that are more unusual than conventional droplet-matrix structures. In the case when the contact angle of the particles measured through the continuous phase is small (but still far from zero), an unusual morphology dubbed a bridged Pickering emulsion gel has been noted in both oil/water (Fig. S15)(70) as well as polymeric systems (Fig. S16)(21). In this case, a monolayer of particles is sandwiched between two drops, holding a stable film of the preferentially-wetting fluid separating the drops(71-75). Fig. S15 corresponds to a small-molecule system with a relatively high loading (8-18 vol%) particles, and a high surface coverage is reached. In this case, the drops deform into polyhedral shapes resembling foams. Fig. S16 corresponds to a polymeric system with much lower (~ 1 vol% or lower) particle loadings. At the lowest particle loadings, the surface coverage of the particles is not adequate to cover the entire surface of the particles. In this case, the polyhedral shapes do not appear; instead the particles partition into the contact region between the drops, leaving much of the drop surfaces bare. Similar results have been shown by Horozov(21, 74). We emphasize that Fig. S15 and S16C&D and elsewhere(71-75), the drops are flattened against each other even though they are not crowded, e.g. in Fig. S15a, drop volume fraction is less than 0.2. Instead the drops are flattened against each other because the bridged particles constitute an attractive force between the drops which can overcome their capillary pressure. In both cases, such mixtures tend to show gel-like rheology since the drops are glued together. We emphasize that while bridging requires the contact angle to be far from 90° , it must also be sufficiently far from zero. If the contact angle is too close to zero, then one reverts back to the fully-wetting situation discussed in the earlier part of this Supplementary Material.

Next we turn to the special case of bicontinuous structures. Surfactant-free small molecule mixtures do not show bicontinuous structures readily. However, when a homogeneous binary mixture (without particles) is quenched into the two phase region, phase separation occurs *via* spinodal decomposition, and if the phase volume ratios are roughly equal, bicontinuous morphologies results. These usually coarsen and often break into dispersed phase morphologies. However addition of particles that are equally-wetted by both phases can arrest phase separation to give a *bijel*(76). A bijel was already evident in Fig. S14b. A more detailed example is shown in Fig. S17. Fig. S17a examines mixtures in which the two phases had nearly equal volumes. While structural arrest (as evidenced by non-spherical interfacial shapes) can

happen at very low particle loading, at particle loadings exceeding 1.6%, true bicontinuity can be reached. Fig. S17b shows fixed particle loadings across a range of fluid volume ratios and emphasizes emphasizes that bijels appear only the two fluids have nearly equal volumes(77). Similar bijels have been realized by spinodal decomposition in other systems including polymers(78-81).

In contrast to small-molecule systems, blends of immiscible homopolymers even in the absence of added particles, show bicontinuous structures near phase inversion(82). Bicontinuity may be flanked on both sides by highly elongated or fibrillar structures which become increasingly interconnected as true bicontinuity is approached. In many instances, interfacially-adsorbed particles are recognized to stabilize bicontinuous(83-86) or other highly non-spherical morphologies against coarsening(21, 87, 88). However when one considers not merely quiescent stabilization against morphological coarsening, but the formation of bicontinuous morphologies or of highly elongated structures, the effects of interfacial particles appear to be more complex. For instance, Fig. S18(20) illustrates an example in which the particle-free two-phase morphology consists of spherical drops of one polymer dispersed in another. Addition of particles first induces the formation of highly elongated structures that are interfacially-jammed. At higher particle loadings however, the dispersed phase reverts to less elongated (although still interfacially-jammed) shapes. Similar transition to highly elongated structures has also been noted by Tong et al.(88) At least one publication(86) has noted that particles increase the range of compositions over which bicontinuity is realized.

All the discussion in this section thus far was restricted to relatively low particle loadings, typically under 10 vol%, and often under 2 vol%. The literature on the behavior at higher particle loadings is sparse. Koos et al(89) have examined the rheological behavior of three-component systems with partially-wettable particles across a wide range of fluid volume ratios at particle loadings up to 30 vol%, however structural characterization was reported only when the one of the fluids was very dilute. One remarkable result from this research is that even drops that do not preferentially-wet the particles can glue together the particles into a space-spanning network illustrated in Fig. 3g in the main text. The building blocks of this network are believed to be clusters composed of several particles held together by a single drop(90). In a sense, the cluster resembles a typical particle-coated drop from a Pickering emulsion except that the drops are comparable in size to the particles, i.e. Fig. 3g and h differ only in the size of drops relative to the particles. In the same sense, the network of clusters is analogous to a particle-bridged Pickering emulsion gel, and both show gel-like rheology.

Finally we turn to the special case when one of the fluids is air. Fig. S19 shows the structure of air/water/hydrophobic particle systems mixed by shaking all components together(5). A remarkable

phenomenon of transitional phase inversion is observed as the wettability of particles is changed: highly hydrophilic particles remain dispersed in water (with air being excluded completely), somewhat-hydrophobic particles stabilize foams (with air as the dispersed phase), whereas highly hydrophobic particles stabilize liquid marbles (with air as the continuous phase). This figure is analogous to Fig. S11, but with the oil replaced by air. Similar to oil/water systems, in the air/water system too, transitional inversion can be induced by addition of surfactant or by changing pH, or by changing the polarity of the oil(91-93). This last example is illustrated in Fig. S20 which shows liquid/air/particle mixtures realized using the same particles, but a variety of non-aqueous liquids(91). The various liquids have different wettability towards the particles; liquids with relatively good wettability towards the particles form foams (Fig S20a), but the foam stability becomes poorer as the wettability becomes poorer. Once the liquid becomes sufficiently poorly-wetting towards the particles, inversion into a powdered liquid happens (Fig. S20c), which is transitional inversion. Catastrophic inversion can also be induced by changing the air/water ratio (91, 94), which is also analogous to oil/water systems.

Particle-stabilized dry liquids or liquid marbles have been reported in a variety of other systems(4, 95-97), and many more articles can be found in recent reviews(98, 99). Numerous particle-stabilized foams have also been reported(94, 100-105), including with molten plastics(106, 107). In summary, liquid/air/particle mixtures behave similar to liquid/liquid/particle systems with the exception that bicontinuous morphologies do not appear when one fluid is air.

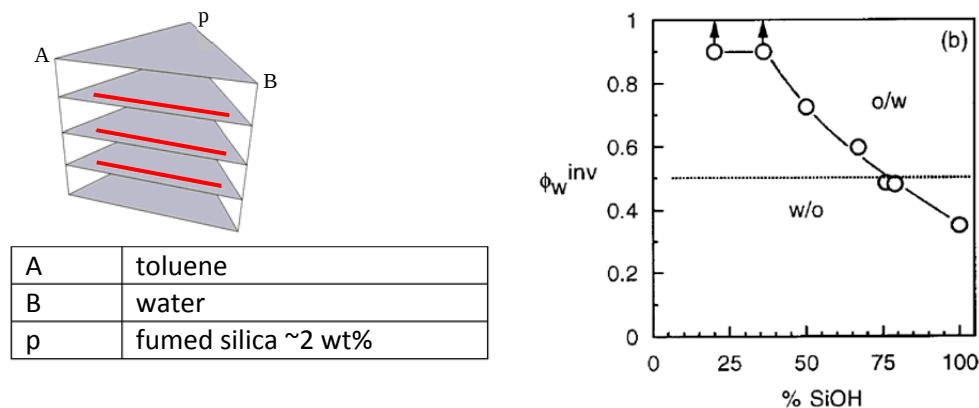


Fig. S11: Phase continuity of emulsions at various water:toluene ratios as the particle wettability changes. Hydrophilicity of the particles increases with increasing % SiOH, with 100% SiOH being fully-hydrophilic. "o/w" denotes oil-in-water, and "w/o" denotes water-in-oil. The y-axis is the volume fraction of water for emulsion inversion. Vertical arrows indicate that the volume fraction of water for inversion is higher than 0.9. Horizontal line denotes equal volumes of oil and water. Reprinted with permission from Ref. (46), Binks & Lumsdon (2000) Influence of particle wettability on the type and stability of surfactant-free emulsions. *Langmuir* 16:8622, Copyright (2000) American Chemical Society."

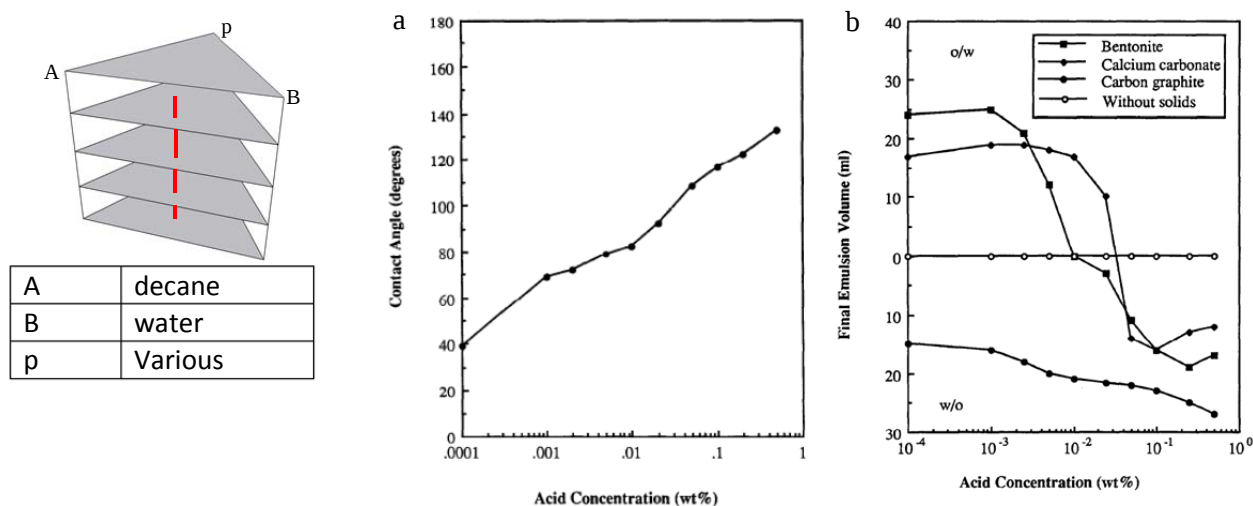


Fig. S12: (a) Decane/water contact angle (measured through the water phase) on the flat surface of a calcium carbonate crystal. The calcium carbonate becomes increasingly hydrophobic as stearic acid concentration increases. Phase continuity of emulsions of decane and water (15 ml each) as stearic acid concentration is varied. Y-axis plots the quantity of the emulsion (maximum 30 ml), with positive values being oil-in-water, whereas negative values being water-in-oil. Note that the inversion from oil-in-water to water-in-oil for the calcium carbonate particles in (b) correlates with a 90° contact angle in (a). Note also the poor emulsion stability near phase inversion. Figure reprinted from Ref. (45), Tambe & Sharma (1994) The Effect of Colloidal Particles on Fluid-Fluid Interfacial Properties and Emulsion Stability. *Adv. Colloid Interface Sci.* 52:1, Copyright (1994), with permission from Elsevier.

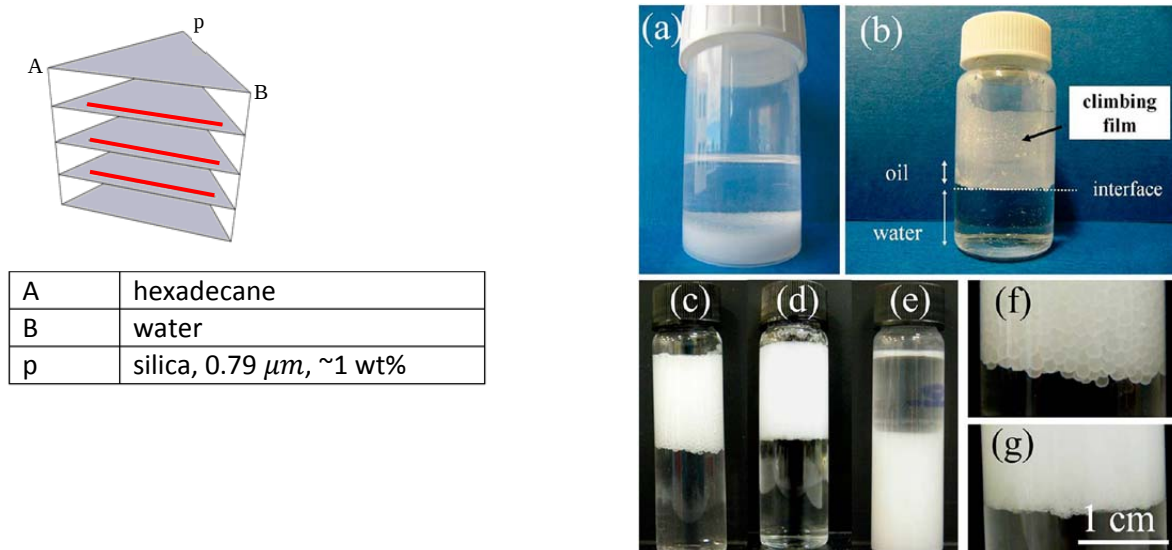


Fig. S13: Structure of oil/water/particle mixtures(63) with changes in wettability effected by changing pH (the particles have a pH-sensitive coating). (a) Water-in-oil emulsion with sedimented water drops with relatively hydrophobic particles. (b) At roughly 90° contact angle, the emulsion is unstable and displays film climbing(108)(109). (c&d, and corresponding close-up views in f&g): Relatively hydrophilic particles give oil-in-water emulsions with creamed oil drops. (e) Highly hydrophilic particles remain suspended in water leading to complete separation. Reprinted with permission from Ref. (63), Destribats et al (2014) Pickering Emulsions: What Are the Main Parameters Determining the Emulsion Type and Interfacial Properties? *Langmuir* 30:9313, Copyright (2014) American Chemical Society.

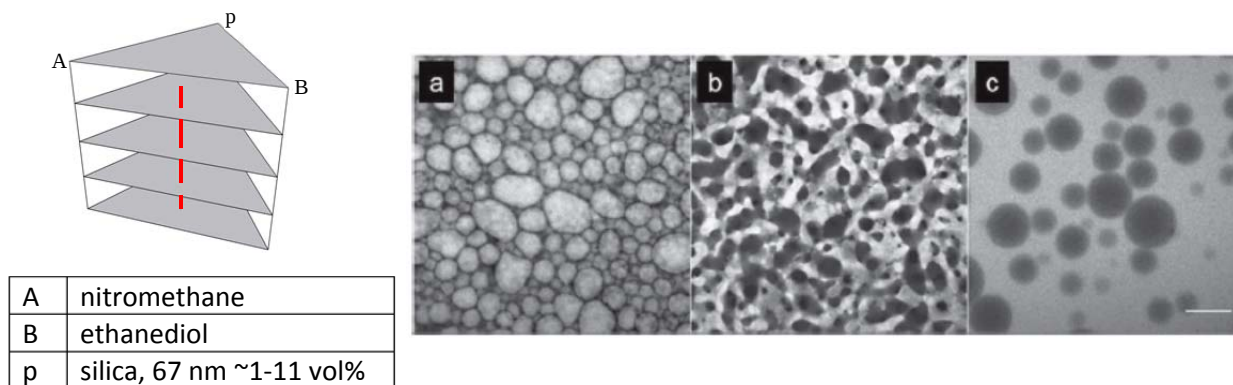


Fig. S14: Structure of nitromethane/ethanediol/particle mixtures with changes in wettability effected by chemically-tethering a hydrophobic group on the particle surface(109). In all three images, the composition is same (and the two fluid phases are at nearly equal volume). In (a), the particles are preferentially-wetted by the ethanediol which becomes the continuous phase. In (c), the particles are preferentially-wetted by the nitromethane which becomes the continuous phase. (b) corresponds to neutral wetting by both phases and a bijel is realized. The scale bar is 100 μm . Images reproduced from Ref. (109), Tavecchi et al (2011) Novel, Robust, and Versatile Bijels of Nitromethane, Ethanediol, and Colloidal Silica: Capsules, Sub-Ten-Micrometer Domains, and Mechanical Properties. *Adv. Funct. Mater.* 21:2020, with permission from Wiley.

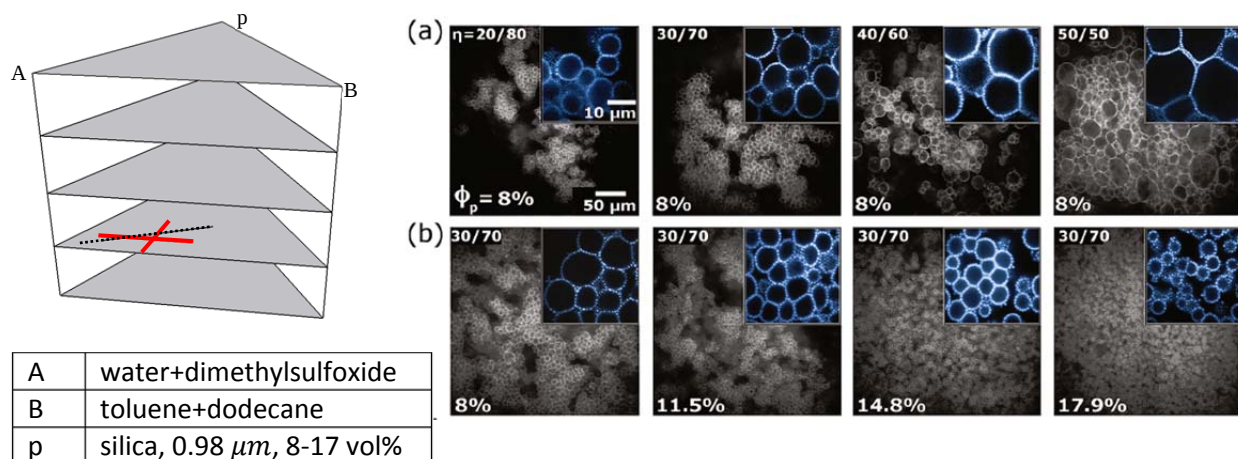
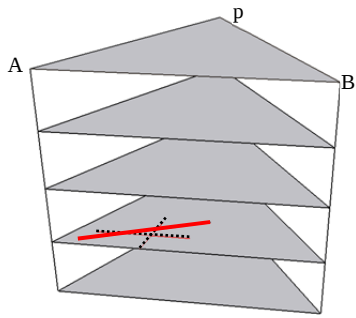


Fig. S15: Confocal microscopic images of the structure of aqueous/oil/particle mixtures containing highly hydrophobic particles(70). (a) varying the water:oil ratio (η) while keeping particle loading fixed at 8 vol%. (b) varying particle loading at a fixed water:oil ratio. The particles are fluorescently tagged. In the insets (which are higher magnification images), note that a single layer of particles separates the polyhedral drops. Images reproduced from Ref. (70), Lee et al (2012) Characteristics of Pickering Emulsion Gels Formed by Droplet Bridging. *Langmuir* 28:3085, Copyright (2012) American Chemical Society



A	polyethylene oxide
B	polyisobutylene
p	silica, 2.7 μm , 0-3.5 wt%

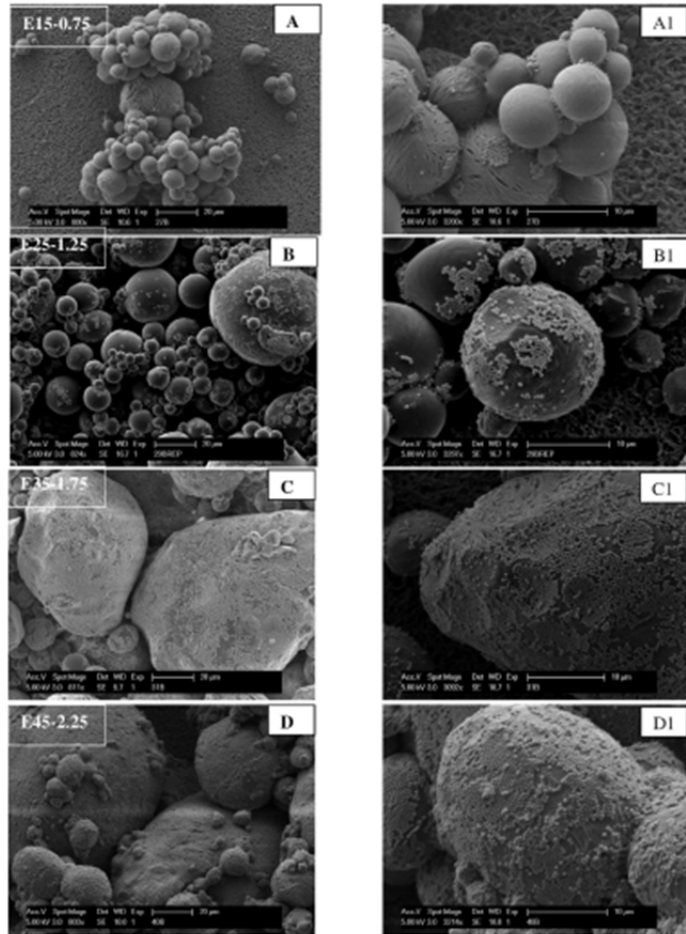


Fig. S16: Structure of polymer blends with changing composition when the particles are preferentially-wetted by the polyisobutylene continuous phase(21). The polyisobutylene phase has been removed by selective dissolution prior to imaging. The top left sample labeled E15-0.75 has 15 wt% polyethylene oxide and 0.75 wt% particles, and the same convention is followed for all samples. Right column images have higher magnification than left column. The scalebars are 20 μm in the left column, and 10 μm in the right column. Note the bridging particles in A1, and the concave regions in many images where a previously-attached drop has fallen away during sample preparation. Reproduced from Ref. (21), Nagarkar & Velankar (2012) Morphology and rheology of ternary fluid-fluid-solid systems. *Soft Matter* 8:8464, with permission from The Royal Society of Chemistry.

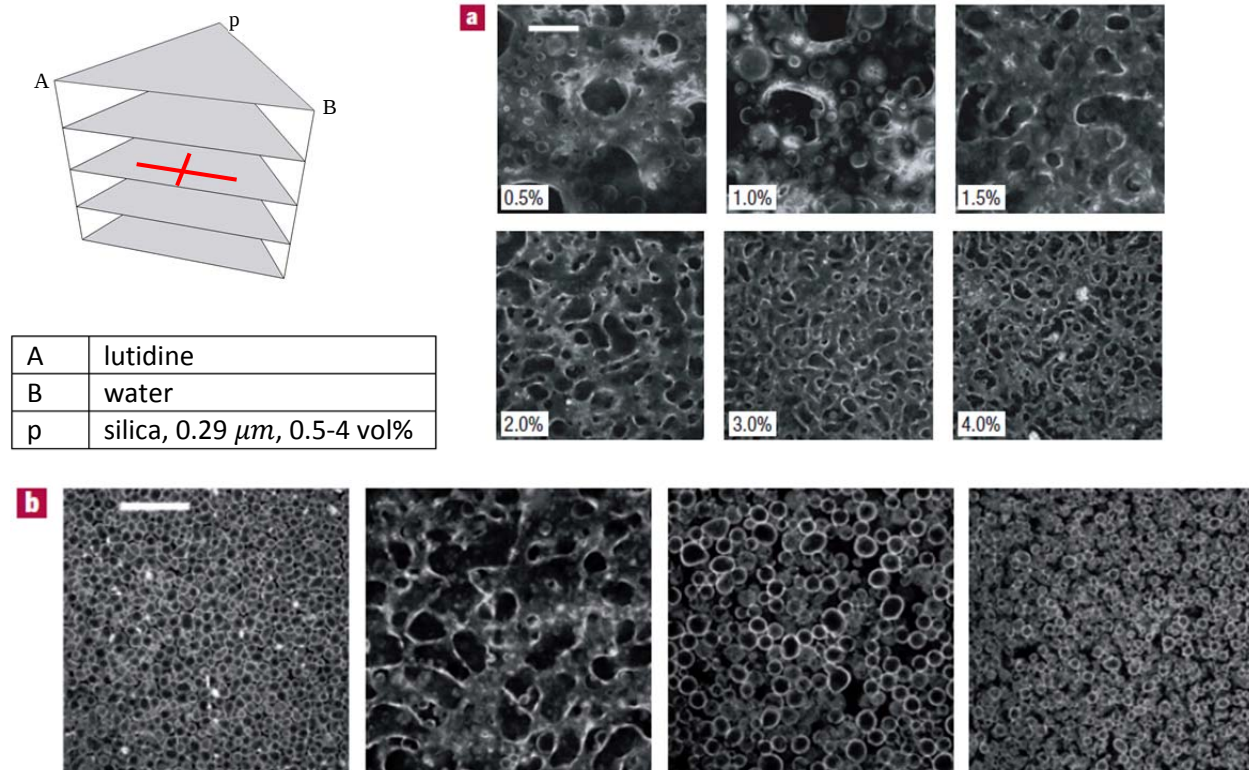
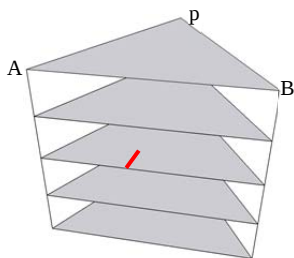


Fig. S17: (a) Stabilization of bijels at various particle loadings (numbers at bottom left of each image are particle volume fraction). Note the decreasing lengthscale of the bijel as particle loading increases. (b) Destruction of bijels as the volumes of the two phases becomes unequal(77). Only the second image from the left has the two phases at roughly-equal volume. The scale bar is $100 \mu\text{m}$ in both images. Reprinted from Ref. (77) by permission from Macmillan Publishers Ltd: Nature Materials, Herzig et al. (2007) Bicontinuous emulsions stabilized solely by colloidal particles. *Nat. Mater.* 6:966, copyright (2007).



A	polyethylene oxide
B	polyisobutylene
p	silica, 2.7 μm , 0-3.5 wt%

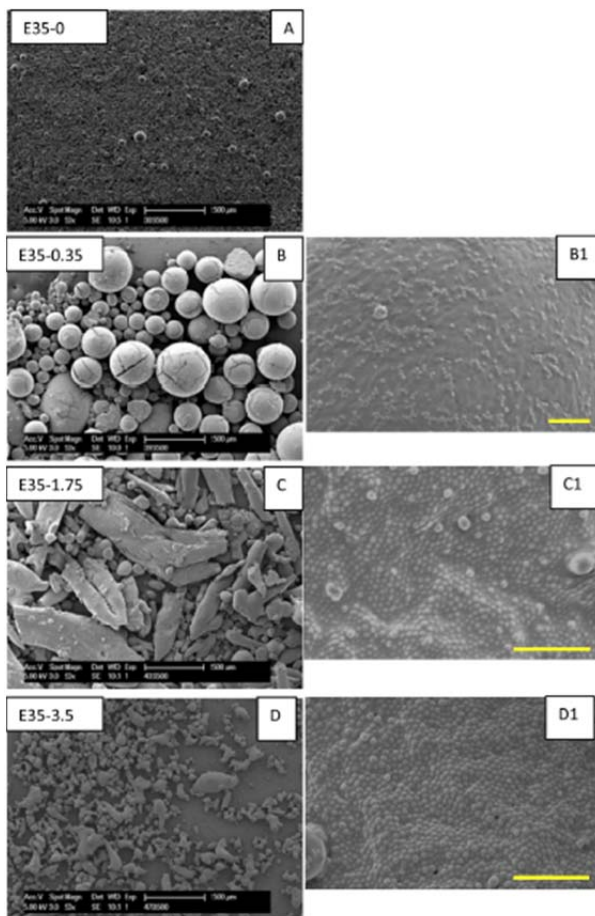


Fig. S18: Structure of polymer blends with changing composition when particles are roughly equally-wetted by both phases(20). The top left sample labeled E15-0.75 has 15 wt% polyethylene oxide and 0.75 wt% particles, and the same convention is followed for all samples. Right column images have higher magnification than left column to show that particles are crowded on the interface in C and D, but not in B. The scale bar is 500 μm in the left column of images and 5 μm in the right column. Images reproduced from Ref. (20), Nagarkar & Velankar (2013) Rheology and morphology of model immiscible polymer blends with monodisperse spherical particles at the interface. *J. Rheol.* 57:901, with permission from AIP Publishing.

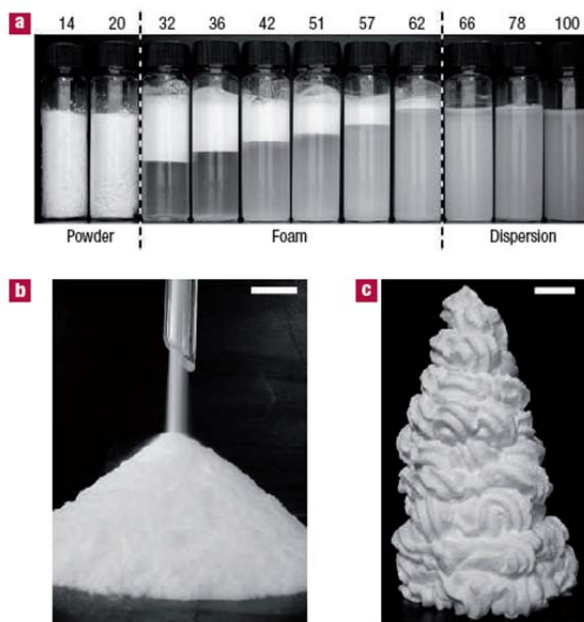
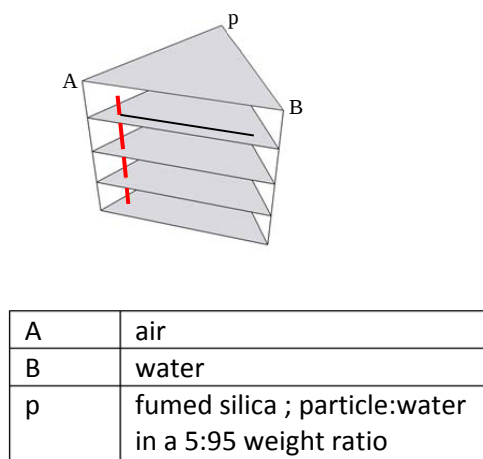


Fig. S19: (a) Changes in structure when an air/water/particle mixture is mixed by shaking. Numbers at the top are the %SiOH groups on the particle surfaces(5). Note that the hydrophilicity of the particles increases with increasing % SiOH, with 100% SiOH being fully-hydrophilic. All samples were prepared with water:air in a 5:95 ratio during mixing, and were then transferred to the vials. (b) Granules of water (also called *dry water*) coated with highly hydrophobic particles (20% SiOH), and (c) particle-stabilized foam from moderately hydrophobic particles (32% SiOH). Scalebars are 10 mm in b and c. Reprinted by permission from Macmillan Publishers Ltd: Nature Materials, Binks & Murakami (2006) Phase inversion of particle-stabilized materials from foams to dry water. *Nat. Mater.* 5:865, copyright (2006).

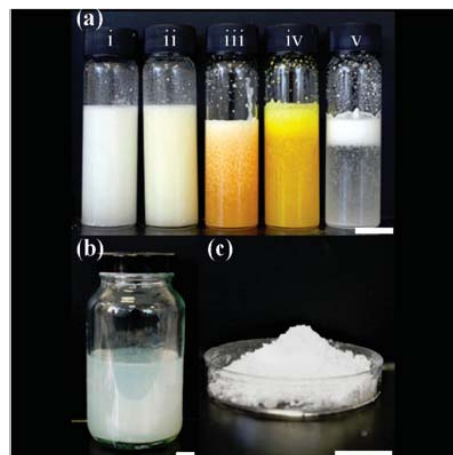
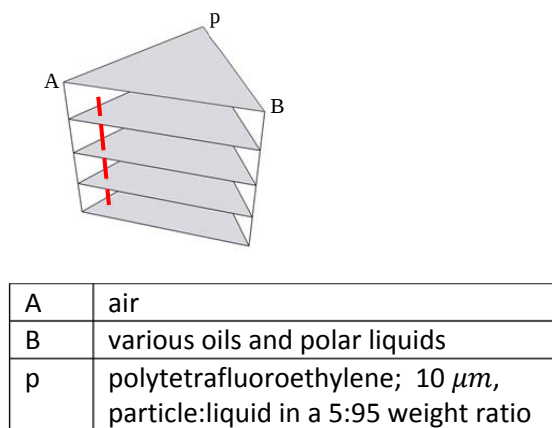


Fig. S20: (a) Structure of particle-stabilized oil foams when the particle-oil-air mixtures are mixed by shaking(91). All the liquids in (a) are relatively-wetting towards the particles, and all form foams. Appearance of mixtures when (b) the liquid fully-wets the particle; here the particles are engulfed by the liquid and stay in suspension. (c) the liquid is poorly-wetting towards the particles, and forms a soufflé-like material which is similar to a powdered liquid. Reproduced from Ref. (91), Binks & Rocher (2010) Stabilisation of liquid-air surfaces by particles of low surface energy. *Phys. Chem. Chem. Phys.* 12:9169, with permission from the PCCP Owner Societies.

C. Effect of mixing conditions on microstructure

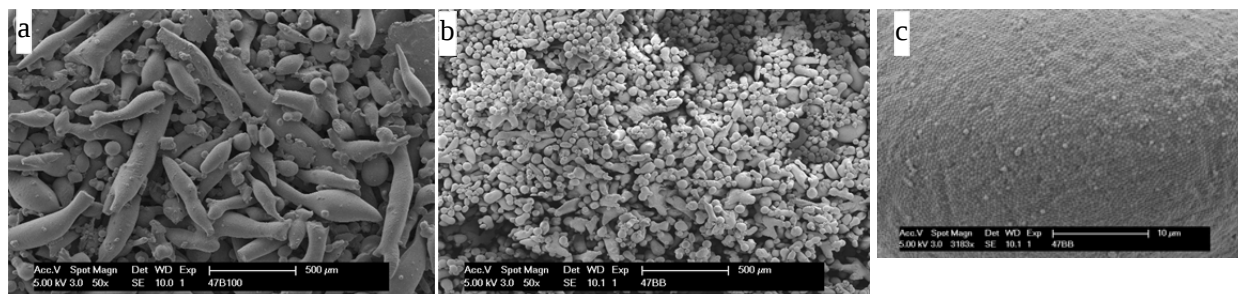


Fig. S21: SEM images of the dispersed phase of blends of polyethylene oxide in polyisobutylene with silica particles. The continuous phase polyisobutylene was removed in a selective solvent before imaging the dispersed phase. Images were taken on blends after a shearing at (a) 100 Pa stress. (b) 500 Pa stress. (c) is magnified image of the surface of (b) showing that particles tightly packed on the interface. Unpublished results from the author's lab, courtesy of Dr. Shailesh Nagarkar.

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