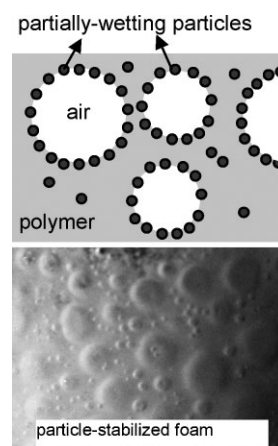Macromolecular
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Polymer Foams Stabilized by Particles Adsorbed at the Air/Polymer Interface

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In aqueous systems, partially hydrophobic particles are known to stabilize foams even in the absence of any added surfactant. This paper shows that the same principle can be applied to polymeric systems: particles that are partially wetted by a polymer melt can stabilize a foam of that polymer. The foam stability is attributable to the adsorption of the particles at the air/polymer interface. Remarkably, stable foams are realized even from polymers that are liquid at room temperature, and hence are otherwise unfoamable. The implications of this result to practical foaming operations are discussed.

Introduction

Polymer foams are commonly used for insulation, cushioning, or for reducing material usage, and hence the weight and cost of plastic parts. This paper is restricted to closed cell foams which are manufactured by generating gas bubbles in a liquid matrix (either a molten polymer or reacting monomers), and then solidifying the matrix so as to trap the gas bubbles.[1,2] During the foaming process, the cell walls separating adjacent bubbles can rupture, causing cell coalescence, and eventually foam collapse. Stabilizing the polymer foam requires that the polymer matrix be solidified by vitrification [e.g., polystyrene (PS) foams], cross-linking (e.g., polyurethane foams), or crystallization (e.g., polyethylene foams); we are unaware of any polymer foams that remain stable for extended periods if the polymer matrix remains a liquid.

The situation is quite different in aqueous systems: common experience suggests that a stable foam can be realized even from a fully liquid system comprised of water and liquid surfactant. In this case, the surfactant adsorbs at the air/water interface causing effects such as Marangoni stresses and interfacial dilational elasticity which stabilize the foam. There have also been several recent examples of aqueous foams stabilized by partially hydrophobic particles.[3–9] Such particles adsorb at the air/water interface and form a rigid shell ("armored bubbles"[10]) that protects bubbles against coalescence. Foaming studies in non-aqueous systems are less common, but interfacially adsorbed particles can stabilize foams in non-polar oils as well.[11]

The effects mentioned in the previous paragraph (Marangoni stresses, dilational elasticity, a shell of adsorbed particles) are all *interfacial* in nature, i.e., unlike polymer foams, aqueous foams are stabilized by interfacial mechanisms. This immediately raises the question: is it possible to stabilize a polymeric foam by an interfacial mechanism? Here, we will show that interfacially adsorbed particles can indeed stabilize foams of polymers that cannot be foamed otherwise. Thus, we show that interfacially

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adsorbed particles can help advance the technology of polymeric foams, just as they have recently helped advance metallic[12–14] and ceramic[15] foam technology.

Experimental Part

Materials' Selection

A particle that is partially wetted by a liquid can adsorb at the air/liquid interface. Interfacial adsorption of a large number of such particles can cause a monolayer to develop at the air/liquid interface, and the significant mechanical robustness of such a monolayer is then responsible for foam stabilization.[3–9]

A common rule of thumb is that solid particles adsorb at an air/liquid interface if the surface energy (i.e., surface tension) of the liquid exceeds that of the particles.[16] This rule suggests that for polymer foam stabilization, one should select particles of low surface energy, and a polymer melt of higher surface energy. Since PTFE is regarded as a low-surface energy polymer, PTFE particles (Dyneon TF 9205; see Figure 1a) were selected. Their surface energy was estimated by a "float-sink" test[17,30] to be $\gamma_p = 25–28.5$ mN $\cdot$ m^{-1}.

This research was conducted using three polymers (see Table 1 for details), all of which were selected for their low viscosity, which allows the particles to be blended by hand-mixing (this would not be possible with typical thermoplastic polymers of much higher viscosity). The first two polymers, polyisobutylene (PIB) and polydimethylsiloxane (PDMS), are liquid at room temperature. The surface tension of PIB exceeds γ_p, and hence PTFE particles are expected to adsorb at the PIB/air interface. In contrast, the PDMS serves as a negative control; the surface tension of PDMS is lower than γ_p, and hence the particles are not expected to adsorb at the PDMS/air interface. Finally, PIB and PDMS, being liquid at room temperature, are not suitable for scanning electron microscopy (SEM) imaging of the foams. To enable SEM imaging, PS, whose surface energy also exceeds γ_p, was selected. A polystyrene (PS) with a low molecular weight (and hence a low T_g of $\approx$35 °C) was chosen so that it would become molten upon modest heating, allowing the particles to be blended in by hand.

Sample Preparation and Foaming

A chemical blowing agent azobisformamide (ADC/L-C2 supplied by Lianda Corp., Ohio, USA) was used for foaming. This blowing agent is available in the form of a powder of $\approx$3 μm particles, and upon heating to approximately 195 °C, decomposes to release nitrogen.

0.2 wt.-% blowing agent and 5 wt.-% PTFE particles were dispersed into each of the three polymers by hand-blending with a spatula, and degassed in vacuum. For PIB and PDMS, samples were blended at room temperature, whereas for PS, hand-blending was conducted at 75 °C. Control samples that contained no PTFE particles were prepared by the same procedure.

Each of the three dispersions was charged into glass vials. The vials were suspended in an oil bath preheated to 180 °C, a temperature at which decomposition rate of the blowing agent is negligible. The temperature of the oil bath was then raised to 195 °C over 8–10 min to induce decomposition of the foaming agent.
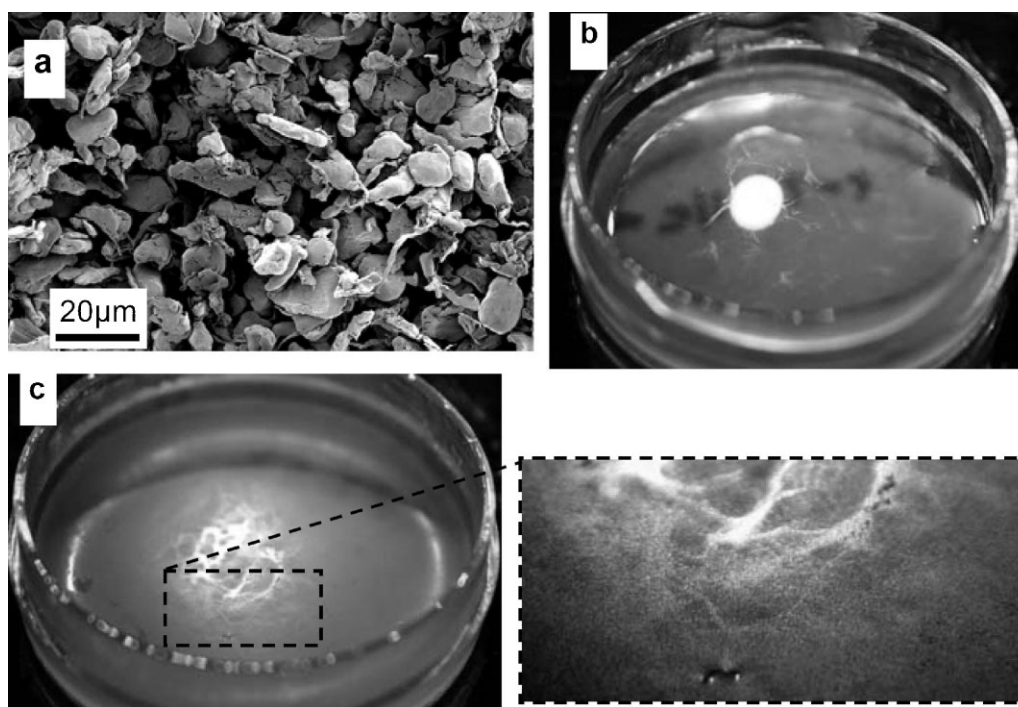

Figure 1. (a) SEM image of PTFE particles. (b) 5 wt.-% PTFE in PDMS dispersion shows a smooth surface. The white spot at the center of the petridish is the light source reflected from the air/PDMS surface. (c) 5 wt.-% PTFE in PIB dispersion shows a matte surface due to an adsorbed layer of particles. The matte texture is clearer in the inset.

Table 1. Homopolymers and their properties.

Polymer	Supplier	MW	Viscosity	Density	Surface tension
		kg · mol^{-1}	Pa · s	kg · m^{-3}	mN · m^{-1}
Polydimethylsiloxane (PDMS)	Rhodia	136	100 at 25 °C	960	19.2[a]
Polyisobutylene (PIB)	Soltex	2.4	333 at 25 °C	910	32.1[a]
Polystyrene (PS)	Eastman Chemical	1.3	170 at 85 °C	1050	40.7[29]

[a]Measured at room temperature by the pendant drop method.

Results

Particle Adsorption at Air/Polymer Interfaces

Before conducting foaming experiments, we first tested the predictions of the rule of thumb stated in the Section "Materials' Selection," *viz.* that PTFE particles will adsorb at the air/PIB interface, but not at the air/PDMS interface. 5 wt.-% PTFE particles were dispersed into PIB and PDMS (no blowing agent was added), and the dispersions were degassed. Visual observation of the degassed samples reveals a significant difference between the two samples. As expected, the PTFE-in-PDMS dispersion had a mirror-smooth surface typical of a liquid (Figure 1b) indicating that the PTFE particles were not adsorbed at the air/PDMS interface. In contrast, the surface of the PTFE-in-PIB dispersion (Figure 1c) appeared to have a "matte" texture because it was covered with adsorbed PTFE particles. It must be emphasized that the density of the particles ($\approx$2 200 kg · m^{-3} for bulk PTFE) far exceeds that of PIB as well as that of PDMS. Thus, the fact that particles are present at the air/PIB interface but not at the air/PDMS interface cannot be attributed to buoyancy forces, and must be attributed to the differences in wettability: PDMS wets the particles fully, whereas PIB does not.

Stable Foams from Liquid Polymers

Based on the above results for particle adsorption, it may be hypothesized that the particles can stabilize a PIB foam, but not a PDMS foam. Foaming experiments were conducted as described in the Section "Sample Preparation and Foaming." In the case of the PTFE/PDMS dispersions, gas bubbles were observed to rise to the surface and burst, and hence—as expected—a stable foam was not realized. Figure 2a shows that not a single bubble survives at the end of the foaming process. In contrast, in the case of the PTFE/PIB dispersions, while the bubbles still rose to the top, they did not burst, but instead accumulated to form a stable foam (Figure 2b). We believe that as the gas bubbles rise upwards, PTFE particles adsorb on the surface of the bubbles. We hypothesize that early in the process, these adsorbed particles do not prevent coalescence. However, as coalescence proceeds, the interfacial concentration of particles grows sufficiently large that coalescence of
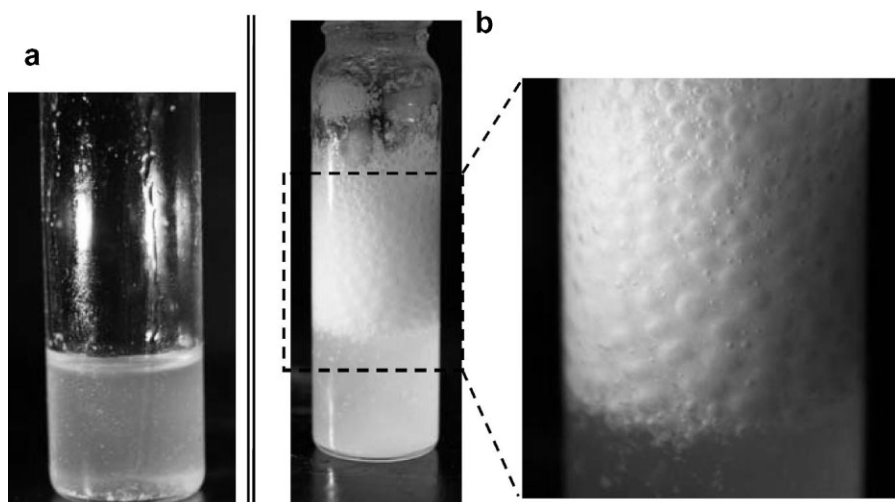

Figure 2. (a) PFTE/PIB dispersion after decomposition of blowing agent. No foam survives. (b) Stable foam of PTFE/PIB dispersion formed after decomposition of blowing agent. Note that (b) was taken after cooling to room temperature. Such cooling causes shrinkage (see text) and hence the foam volume in this image is less than that at the end of the foaming process.

bubbles is suppressed altogether. Upon cooling the PTFE/PIB foams to room temperature, contraction of the gas trapped in the bubbles causes the foams to shrink. Nevertheless, the foams did not collapse even after several months.

The above procedure was also repeated with a dispersion of the blowing agent in PIB in the absence of PTFE particles. In this case, the gas bubbles escaped from the vial and stable foams were not realized.

Particle-Scale Imaging Particle-Stabilized Foams

Since the PIB is liquid at room temperature, it is not possible to undertake a detailed SEM characterization of PIB foams on the scale of single particles so as to directly examine the stabilizing monolayer. To enable SEM imaging, it is essential to realize particle-stabilized foams from a polymer that is solid at room temperature, and as explained in the Section ''Materials' Selection,'' PS was used for this purpose. PS samples without PTFE particles did not give stable foams; the gas bubbles generated by decomposition of the blowing agent rose and escaped from the top surface of the sample. In contrast, a stable foam was realized from the PTFE/PS samples, furthermore, the foam did not collapse when the sample was maintained at 195 °C (i.e., with PS staying molten) for 5 min. In summary, the PTFE/PS system behaved similar to the PTFE/PIB system, but with the advantage that upon cooling to room temperature, a solid foam was obtained. Unfortunately, the solid foam was fragile and could not be recovered intact from the vial.

In order to facilitate recovery of the PTFE/PS foam, the foaming experiment was repeated with the inside of the vial covered in aluminum foil. Upon foaming and then cooling, the cylindrical sample of foam, still wrapped in aluminum foil, was successfully recovered from the vial, fractured, and examined under SEM. Figure 3a, which is a low magnification image of the cross-section of the fractured foam, shows several bubbles embedded in the matrix. Higher magnification reveals that different bubbles have a wide range of particle coverages; e.g., one of the bubbles in Figure 3b is heavily covered with particles, whereas the other is only sparsely covered. Figure 3c shows the particle-scale image of the inside of a foam bubble; it is clear that a portion of each particle is embedded in the PS phase, and the remainder emerges into the gas bubble. This strongly suggests that particle adsorption is indeed attributable to the partial wettability of the particles toward the polymer. The SEM images also suggest that some PTFE particles are not adsorbed on the interface, but still remain in the bulk PS. Furthermore, the bubbles in the PTFE/PS foam of Figure 3a do not appear to be impinged upon each other but instead are well spaced. These observations suggest that the particles in the bulk
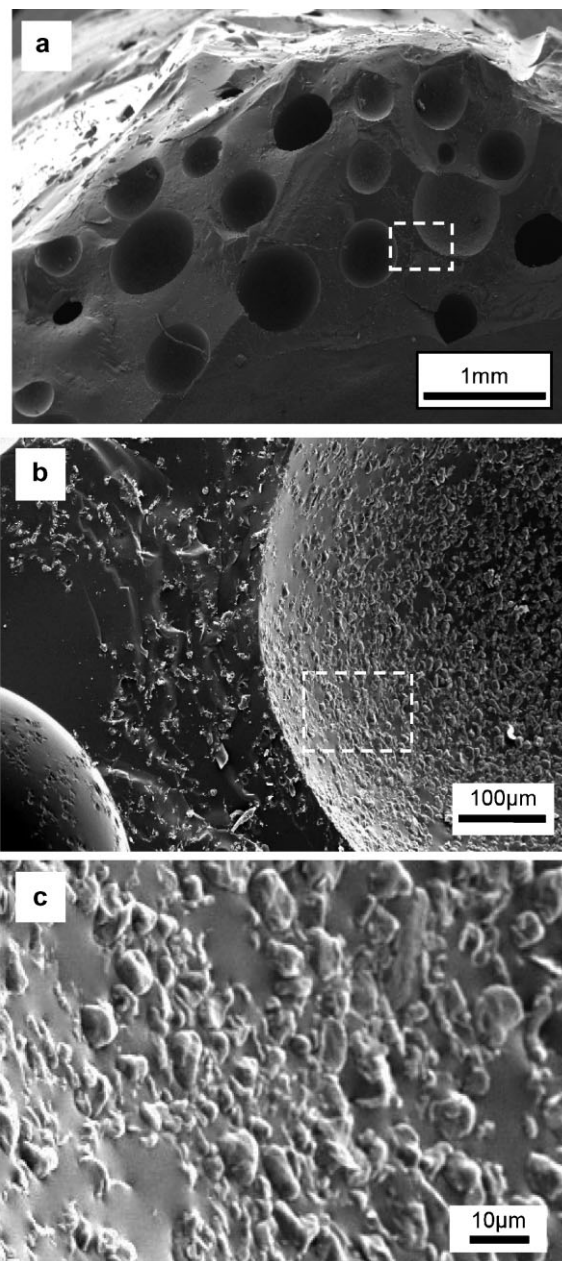

Figure 3. SEM images of fractured PS foams cooled to room temperature. The dotted white rectangle from (a) is magnified in (b). The dotted white rectangle of (b) is magnified in (c).

may contribute to foam stability by keeping the bubbles far apart; more comments on the bulk effects of particles will be made at the end of this paper.

Discussion and Implications

To summarize, the chief experimental observations are:

(i) None of the three polymers, PIB, PDMS, or PS could be foamed in the absence of added PTFE particles.

(ii) Addition of PTFE particles led to PIB and PS foams. These foams were stable for extended periods even when the PIB or PS were maintained in the liquid state.

(iii) Addition of PTFE particles did not lead to PDMS foams. This observation strongly supports the idea that the foam stabilization mechanism is interfacial in nature; if the particles do not adsorb at the air/polymer interface (as is the case with PDMS), they do not enhance foam stability.

(iv) Particle-scale images of the PTFE/PS foams reveal foam bubbles coated with PTFE particles. There is a wide variation in particle coverage from one bubble to another.

The principal result of this paper is that an otherwise non-foamable polymer may be foamed by addition of partially wettable particles. Specifically, the partially wettable particles can adsorb at the air/polymer interface and confer long-term stability on a polymer foam even when the polymer itself remains molten. This is of much relevance to preventing cell coalescence and foam collapse in practical foaming operations. For example, it is well recognized that for successful foaming, a polymer must have sufficient melt elasticity. Some polymers, most notably linear polypropylene, have poor melt strength, and hence are difficult to foam due to severe cell coalescence during foaming.[2,18–21] Accordingly, researchers have investigated the use of branched additives to modify the bulk rheology, e.g., increase the melt strength, and hence improve foamability.[19,20,22] This paper shows that it is possible to use particulate additives for *interfacial* modification (rather than bulk rheology modification) to achieve a similar effect. Furthermore, a possible advantage of this approach is that a low-surface energy additive such as PTFE is non-specific and may be an effective foam stabilizer in a wide variety of polymers. Our results are also relevant to specific polymer processing operations, e.g., rotational molding, in which the processed part must be maintained under melt conditions for extended periods. Incorporating foaming into such processes is challenging since foams can collapse if kept under molten conditions for extended periods.[23–25] In such situations as well, particulate additives offer a convenient method of improving the stability of the foam.

In the experiments described here, relatively large particles were used, and only at a modest particle loading of 5 wt.-%. Practical application of particles as foam stabilizers would likely involve smaller particles since (at a fixed weight loading) smaller particles are likely to have larger interfacial effects. We are presently examining the effect of particle size on foam properties. Furthermore, the SEM images of the PTFE/PS foams suggest that the bubble volume fraction is not very large, i.e., the foams have a relatively high mean density. Experiments in our laboratory are presently addressing this by increasing the concentration of the blowing agent.

Finally, while the focus of this paper has been on the interfacial effects of added particles, it is well recognized that particles can also affect the bulk rheology, especially if they can associate into a percolating network that can cause a yield stress. Such a yield stress would certainly contribute to bubble stability. In the present case, the overall particle loading is only 5 wt.-% (roughly 2.5 vol.-%), and hence at a first glance, bulk rheological changes are not expected. Indeed in the three cases studied here, addition of 5 wt.-% PTFE particles caused no significant change in the rheology (as measured by a rotational rheometer). Nevertheless, the *overall* particle loading may underestimate the bulk rheological effect due to added particles. Specifically, in the two stable foam cases (PTFE/PIB and PTFE/PS) considered above, it is possible that in the top part of the vial where the foam accumulates, the *local* particle concentration in the polymer films separating adjacent bubbles may be larger than 5 wt.-%, and bulk rheological effects may be significant. Such bulk rheological changes may be responsible for the fact that the PTFE/PS foam bubbles appear well separated from each other, and that this foam was stable even though some bubbles appear to be only sparsely covered with particles (Figure 3b). Thus, even if bulk effects are not the primary cause of foam stability, they may still be useful as an additional method to improve foam stability. Indeed there are reports[26–28] on foamed polymer nanocomposites showing that particles such as clay reduce cell sizes in polymer foams. These papers did not note interfacial adsorption of particles, and it may be the bulk rheological effect of added particles that causes foam stabilization.

Conclusion

In summary, this paper shows that — similar to aqueous foams — it is possible to stabilize polymer foams by an interfacial mechanism, *viz.* the adsorption of partially wettable particles at the air/polymer interface. This strategy of foam stabilization appears to be broadly generalizable; the chief requirement is that the stabilizing particles have a lower surface energy than the polymer being foamed. Accordingly, it is possible to foam polymer melts of low melt elasticity, which are otherwise unfoamable. It is also possible to extend the range of conditions under which foaming may be conducted, in particular, permitting processes that maintain the foam under molten conditions for extended periods. Finally, our observations indicate that the particles dispersed in the bulk may also contribute to the foam stability.

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