

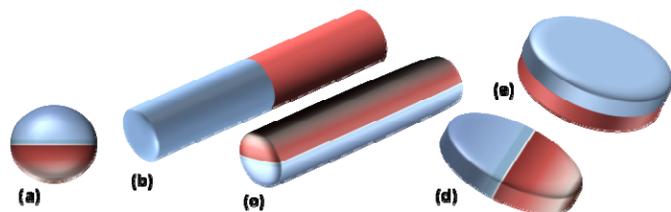
Well-Defined Nanostructured Polymer Blends with Janus Particles

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INTRODUCTION

Janus particles are compartmentalized colloids which possess two sides of different chemistry or polarity. These particles have moved into the focus of various research groups ranging from physics, chemistry to biological science. In general, Janus particles can be divided into several classes according to their architecture and dimensionality (see Scheme 1). The lack of centrosymmetry is inherent to all of these particles and is the major challenging aspect in their preparation.



Scheme 1. Overview of possible Janus particle architectures. (a) spherical Janus particle, (b-c) two types of Janus cylinder and (d-e) two types of Janus discs.

Janus particles are interesting for a variety of reasons, one of them being the self-organization into complex and well-defined assemblies. From a scientific, as well as from an industrial point of view, the advanced surface-active properties of particles with a segregated corona over particles with a uniform wettability are very interesting. Binks et al. calculated that the surface activity of a Janus particle is up to three times higher at an oil/water interface than that of a uniform particle, leading to an enhanced adsorption at the interface.¹ Janus particles uniquely combine the so-called Pickering effect²⁻⁴, known from particles, with amphiphilicity - similar to block copolymers - induced by the Janus character. This combination enables a firm attachment at interfaces and may lead to advanced stabilizing properties in dispersions. Unwanted coalescence of domains of the dispersed phase are thus expected to be diminished using this highly surface-active particles.

Thinking of materials science, nanocomposites, i.e. nanoparticle-filled block copolymers and homopolymers have been attracting increasing interest in the past years. In essence, the controlled dispersion, the precise control of the particle location with the aim of preparing most-well defined nanocomposites has remained a challenging task. A complex interplay between enthalpic and entropic contributions governs the dispersion and location of particles in polymers, block copolymers and polymer blends.

Herein, we will demonstrate two major results. First, a superior performance of Janus particles for compatibilizing polymer blends under high-shear conditions in a twin-screw miniature mixer, utilizing Janus particles on a *multi-gram* scale. Secondly, we will show how to overcome problems in the precise positioning of particles in polymer blends. So far, success in the controlled and exclusive location of particles at interfaces under aggressive conditions remains limited. However, with this approach, we will illustrate that the location of the Janus particles can be effectively controlled on the nanoscale, whereas the processing parameters are applicable to macroscopic production constraints.⁵

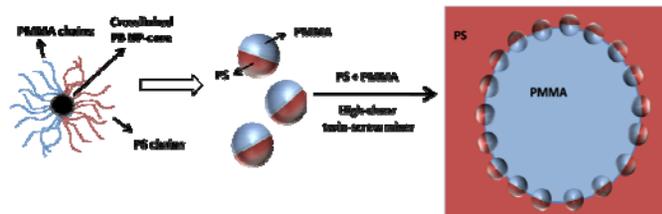
EXPERIMENTAL

Janus Particles. The Janus particles in this study were prepared by crosslinking the well-defined lamella-sphere bulk structure of a polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) (SBM) block terpolymer, having symmetric end blocks and a very small fraction of polybutadiene. Details of this procedure were published earlier.⁶ These Janus particles consist of a tightly crosslinked polybutadiene nanoparticle core with ca. 13 chains each of PMMA (DP = 700) and PS (DP = 800) protruding out of it.

Polymer Blend Preparation. PS/PMMA blends were prepared in a high shear twin screw mixer at 220 °C, by co-mixing PS, PMMA and PS-PMMA Janus micelles. The weight ratio of PS to PMMA was kept constant at 6 to 4 and the amount of Janus micelles was varied.

RESULTS AND DISCUSSION

Polymer Blends. In order to investigate the performance of Janus particles in polymer blends, we blended high molecular weight PS ($M_w = 230000$, PDI = 1.6) and PMMA ($M_w = 120000$, PDI = 1.8) using PS-PMMA Janus particles under high shear conditions in a twin screw mini mixer at 220 °C (Scheme 2).



Scheme 2. Schematic representation of Janus particles and their adsorption at the blend interface of a PS/PMMA blend.

The amount of Janus particles in the mixture was varied to study the effect systematically. Figure 1 depicts TEM images which were obtained after microtome cutting the PS/PMMA blends. When no Janus particles are present as compatibilizer, the blending results in PMMA domain sizes considerably larger than 2 μm . Upon addition of only 1 wt% of Janus particles a significant decrease of the PMMA droplet sizes can be observed. The average domain sizes reach values of around 2 μm and lower. A further increase of the content of Janus particles leads to a further reduction of the domain sizes of the dispersed phase to diameters much below 500 nm. Consequently, the domain size of the minor component can be controlled by the amount of Janus particles added.

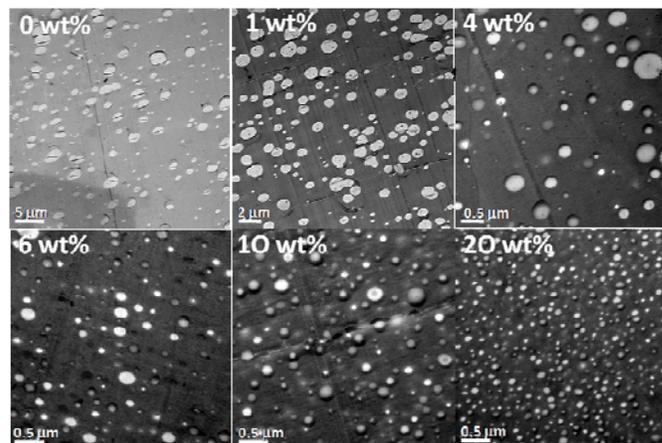


Figure 1. Non-stained TEM images obtained for blends at a PS/PMMA ratio of 8/2 (centre and lower row). The amount of compatibilizer is indicated in each image.

Further analysis of the TEM images also reveals that the Janus particles are located at the interface of the polymer blend. They are well visible as black dots in the magnified image in Figure 2. The size corresponds to the size of a single Janus particle. The interface exhibits a dense coverage of Janus particles, which is the reason for the excellent compatibilization of the two immiscible phases. A careful inspection of the bulk phases does hardly show any Janus particles dispersed in the polymers. Thus, the Janus particles are almost exclusively adsorbed at the blend interface, representing a major advantage compared to standard block copolymer compatibilizers or reactive blending. The enhanced adsorption originates from the amphiphilic character of the particles.

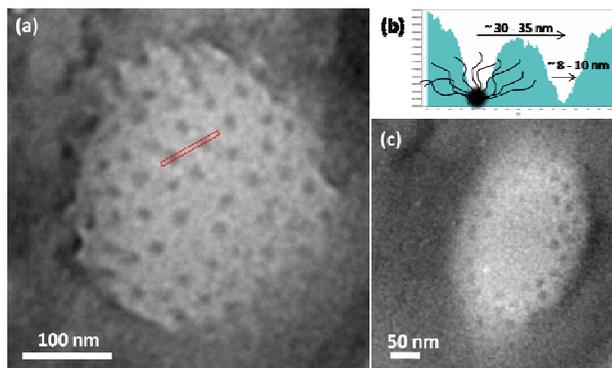


Figure 2. End caps of PMMA droplets with Janus particles located at the interface. (a) and (c) are representative examples at 10 wt% and 6 wt% of JP content in a 6/4 PS/PMMA blend. (b) Section analysis of the red bar shown in image (a). One side of a Janus particle is schematically sketched to show its brush-like character and the location of the polybutadiene core.

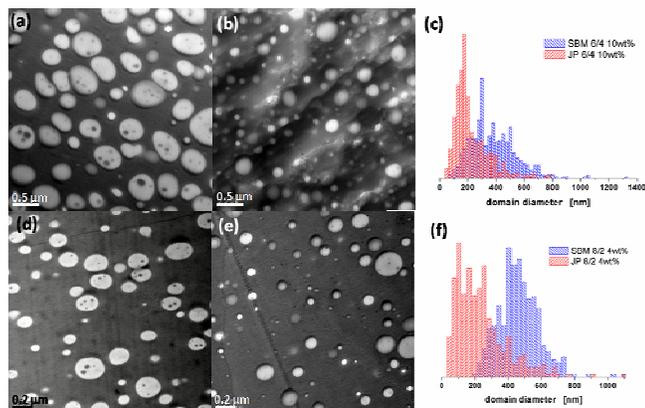


Figure 3. TEM images for polymer blends stabilized with SBM (a, d) and Janus particles (b, e) for different PS/PMMA ratios of 6/4 (first row) and 8/2 (second row). The concentration of the compatibilizer is 10 wt% (a) and 4 wt% (b). The right side shows histograms of the statistical analysis of the PMMA domains.

To compare the performance of our Janus particles with common state-of-the-art compatibilizers, we prepared two series of PS/PMMA blends using a linear SBM (polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate)) block copolymer as stabilizer. The linear block terpolymer used is exactly the same polymer, which is employed for the preparation of the Janus particles. It is of the same composition and has a similar radius of gyration as compared to the Janus particles. Thus, partitioning effects because of different radii of gyration are similar. Therefore, it can be considered as a scientifically correct and fair assessment of the compatibilization efficiency. Similarly to the polymer blends prepared with the Janus particles, the amount of SBM stabilizer was varied for the polymer blends to follow the decay of the domain size of the dispersed PMMA phase in dependence of the

compatibilizer content. Figure 3 displays TEM images and the statistical analysis of the different systems.

At any given concentration, the addition of Janus particles leads to significantly smaller domain diameters, indicating a superior stabilization of the polymer blend system. A more detailed conclusion can be drawn by analyzing the frequency distribution of the domain sizes as shown on the right-hand side in Figure 3. The maximum of the size distribution of the PMMA domains is shifted towards higher diameter when using the block copolymer instead of the Janus particles. The effect is present independently of the stabilizer content and blend ratios used. Consequently, the Janus particles outperform the standard block copolymer greatly.

CONCLUSION

We present the first application study using Janus particles on a *multi-gram* scale. It is shown that Janus particles can be used to efficiently compatibilize polymer blends under high shear conditions. A constant decay of the domain size of the dispersed phase can be observed, independently of the blend composition. The performance of the Janus particles in compatibilizing the polymer blend is significantly superior to other state-of-the-art compatibilizers, such as linear block copolymers. Common problems like micellization of the stabilizer and insufficient adsorption at the interface can be overcome to a major extent. The origin of this continuous decrease is the strengthened adsorption of the Janus particles at the interface, which is in turn caused by their biphasic particle character. In contrast to block copolymers or homogeneous particles, the Janus particles are located at the interface, even at high temperature and shear. The adsorption energy of a Janus particle at an interface at processing conditions is almost as high as for a homogeneous particle at room temperature. This can be explained by an additional enthalpic contribution to the adsorption energy. The Janus particles, adsorbed to the polymer blend interface, exhibit an ordered arrangement. Consequently, the structural order occurs on two levels. The first is the complete adsorption at the interface and the second is the lateral ordering at the interface. This renders them an interesting tool for the nanostructuring of blend and block copolymer interfaces. Therefore, Janus particles provide a mean for the nanoscopic engineering of polymer blend systems, while matching some macroscopic processing constraints.

ACKNOWLEDGMENTS

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