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Particle Morphology of Carboxylated Poly(*n*-butyl acrylate) / Poly(methyl methacrylate) Composite Latex Particles

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SUMMARY: Particles with a copolymer soft core of poly(n-butyl acrylate)/poly(methyl methacrylate) (PBuA/PMMA) and a homopolymer hard shell of PMMA were synthezied by in-situ seeded, two stage polymerization process. The single particle morphology was characterized using transmission electron microscopy (TEM), atomic force microscopy (AFM) and solid-state NMR. The phase ratio as one important parameter was investigated having a strong influence on the particle morphology. A series of core-to-shell ratios from 100/0 (wt%) to 25/75 were synthesized and characterized. The combination of TEM, AFM and solid-state NMR allows quantitative determination of the extent of coverage of the core by the shell polymer and the interphase thickness, both were found to depend on the shell content.

Introduction

Composite latex particles are widely used in industrial applications, e.g., paints, coatings and adhesives, in order to achieve latex or latex film properties which can not be achieved by physically blending two or more different polymer components. The most common process to synthesize composite latex particles is the seeded emulsion polymerization. This technique allows one to create particles in a well defined way regarding the resulting particle size. Using different monomer compositions at different stages in a seeded emulsion polymerization, it is possible to achieve complex particle morphologies by different phase distributions within a particle. The structure of the multiphase particles is influenced by thermodynamic and kinetic factors. The basis for the thermodynamic analysis of multiphase particles was given by Torza and Mason[1] who examined the interfacial behavior of three mutually immiscible fluids and found, that depending on the interfacial tension of the different phases, structures like complete engulfing, partial engulfing or non-engulfing can be realized. These considerations were transferred to the description of multiphase particles by Sundberg et al.[2]. They

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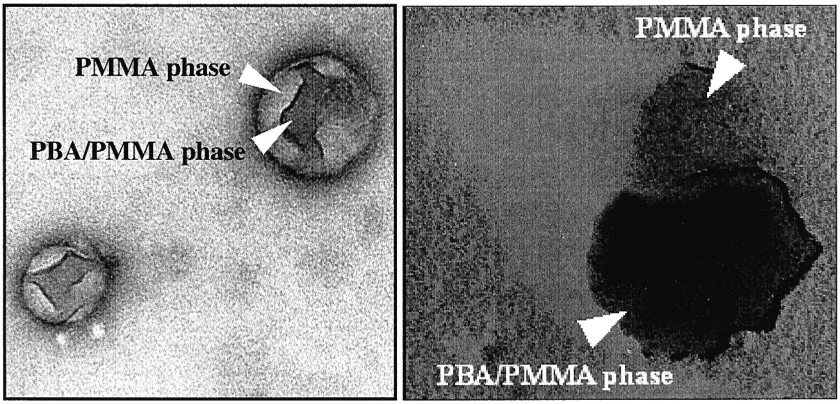
calculated the Gibbs´ free energy of multiphase particles by the equation: $G=\Sigma\gamma_{ij}A_{ij}$ with γ being the interfacial tension between the different polymer phases and water respectively and A being the contact area of the phases i and j. This concept was taken further by El-Aasser et al.[3] who developed a mathematical model to describe free energy differences between different possible particle structures and thus allowing the determination of the thermodynamically most favorable structure of a given system. The interfacial energy between two phases can be influenced by a large variety of parameters. Important factors are monomer composition, emulsifier and initiator. Experimental results reported by several authors were summarized by Rudin[4]. In the work presented here a systematic approach was taken to correlate the structures of multiphase particles to those of their films. Theses results enable us to correlate application properties of the corresponding paints.

Experimental

The latices were prepared by a in-situ seeded, two stage emulsion polymerization process employing a constant amount of sodium dodecylsulfate (SDS) (2.25 pphm) as emulsifier and sodium persulfate (0.3 pphm) as initiator. The polymerizations were carried out at 85 °C. The emulsion feed time was 3 hours. The feed rate was kept constant throughout the polymerization. At the end the dispersions were neutralized by adding sodium hydroxide. The solids content was adjusted to 45 wt.% (details see Ref. 5). The particle size was determined by dynamic light scattering (Nicomp submicron particle sizer (Mod. 370)) and CHDF (1100, Matec Applied Science). No indication of a second generation of particles could be found. The number average particle size of all samples is about 120 nm in diameter. For the TEM experiments a Philips EM400 at an acceleration voltage of 100keV was used. The samples were cleaned by using a filtration unit (Advantec MFS Inc., type UHP-76) to remove all water soluble oligomers from the emulsion. Different staining methods were used described elsewhere[5]. AFM measurements were performed with a Nanoscope Dimension 3000 SPM (Digital Instruments) working in Tapping Mode with phase detection. Si cantilevers with force constants of 35 N/m and resonance frequencies of approximately 300 kHz, (Nanoprobe) were used. For the microscopy of single dispersion particles, the latex was prepared on freshly cleaved muscovite mica surfaces by freeze drying of very dilute dispersions. Films were prepared by drying a thin film at room temperature also using mica as substrate. Advanced solid-state NMR methods based on ^{1}H spin-diffusion experiments have been developed for the characterization of heterogeneities in polymers and polymer blends [6]. These techniques were now applied to the polymer particles. ^{1}H NMR solid-state spectra were recorded on a General Electric GN-300 NMR spectrometer equipped with a standard Doti MAS probe head.

Results and Discussion

Different methods of imaging the latex particles by **TEM** were used: (i) Preferential staining of the PBA/PMMA soft phase with RuO_4. To prevent the latex particles from beam damage, the samples were also negatively stained with UAc before exposing them to the RuO_4 vapor. (ii) To distinguish between soft and hard phases, the particles were shadowed with Pt-shadowing/casting. An example is shown in Figure 1 for the 65/35 latex particles with an soft to hard phase ratio of 65 to 35. From Figure 1(a) it is obvious that the soft phase (slightly stained by RuO_4) is covered by the PMMA hard phase (not stained). In Figure 1(b) a similar sample was investigated by the Pt-shadowing technique. From the picture it is obvious that the different phases of the 65/35 particle separate into two parts during the drying process. The small, light gray area, having a long shadow corresponds to the former hard phase of the particle. The part of higher contrast has a relatively short shadow length corresponding to the soft phase.

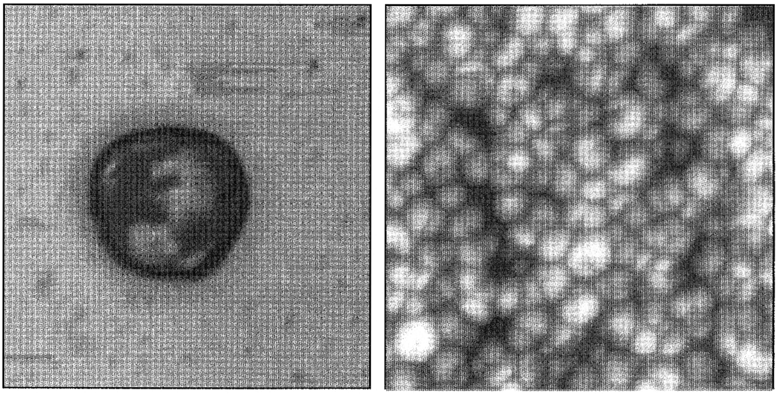


(a) (b)

Fig. 1: (a) 65/35 particles stained by RuO_4. The inner dark phase represents the n-BA rich soft phase. The outer, not stained, polymer phase represents the PMMA hard shell. (b) Same particle type investigated by Pt-shadowing technique.

For this phase, the size ratio (height/broadness) is only about 0.3 which confirms the ellipsoidal shape of that phase during the shadowing process. The sizes can only be estimated due to the difficulty in evaluating the proper particle size because of the superposition of both shadows from the soft as well as from the hard phase region in the picture. However, the method of Pt shadowing is an ideal completion to the results of the preferential staining technique. From the results of all samples, we can conclude, that with increasing amount of second stage a core-shell type is more favorite. In this system a stage ratio of 50/50 is required to achieve PBA core- PMMA shell particles.

The **AFM** results on the single particle structure are perfectly in line with the TEM findings as e.g. for the 65/35 particles. A comparison is shown in Fig. 1 a and Fig. 2. The latter gives a phase contrast image of a single dispersion particle, which maps the differences in the viscoelastic and adhesive properties[7] of the two polymer phases present on the particle surface. There is a clear material contrast on the particle between the nBA rich soft phase which appears dark in the image and the PMMA hard shell which appears bright.



(a) (b)

Fig. 2: (a) Phase contrast image of a single 65/35 particle (400 nm x 400 nm). The inner dark phase represents the n-BA rich soft phase. The outer bright polymer phase represents the PMMA hard shell. (b) Height image (1 µm x 1 µm) of the same type of particles investigated as dispersion film.

The topographic image in Fig. 2 b adds further information. Although the 65/35 film is transparent, in the AFM image still the individual dispersion particles are well preserved. This underlines the results from the single particle measurements and directly reflects the partial engulfment of the soft n-BA rich core by the hard PMMA, which effectively shields the cores from strong interdiffusion. This ceases – as expected - for stoichiometries for which the hard phase becomes more localized.

NMR ^{1}H solid-state spin-diffusion experiments were performed at 60°C on freeze dried samples[5]. At this elevated temperature we were able to analyze in one measurement the overall structure of the particle and the interphase structure between first and second stage. From the NMR results we were able to confirm the increasing degree of coverage of the soft phase material by PMMA with increasing amount of second stage material (see table 1). The roughness of the interface has to be taken into account. The NMR results indicate the existence of a core-shell structure for the latexes with a shell content equal to or higher than 35 %. For the latexes with a shell content below 35 %, the shell structure is still incomplete. With increasing shell content, the final value decreases according to a smaller amount of mobile phase in the system. The TEM results show that full coverage is obtained for latexes with a shell content of 50% or higher. The discrepancy of NMR and TEM have two causes. NMR measures an average. This means that if there is a mixture of particles which are covered and particles which are nor yet fully covered, the NMR can see the two different kinds of particles.

Table 1: Surface coverage (%) and volume of interface (%) determined from the spin-diffusion experiment for different core-shell wt ratios

Latex core/shell wt.-ratio	**coverage with roughness [%]**	**volume of interface [%]**
85/15	12	48
75/25	43	50
70/30	43	51
65/35	67	56
60/40	72	57
50/50	100	66
40/60	>100	45
25/75	>100	41

Conclusion

TEM, AFM and solid-state 1H spin-diffusion NMR technique were used to determine different particle morphologies. TEM is able to resolve the particle structure with high spatial resolution even for the P(n-BA/PMMA) latex particles with only small differences in chemical reactivity for staining agents. AFM yields single particle structure through mapping with nanomechanical contrasts – without staining and its potential pitfalls. Furthermore it gives easy access to the film morphology and film formation properties of the latex particles which can be used to further back the model of the particle structure. NMR experiments support the results for the structures seen by TEM and AFM. Furthermore, NMR is a powerful tool to obtain detailed information on the polymer phase distribution inside the particles. Particle morphology of PnBA/PMMA composite latex particles was changed by increasing the phase ratio of the hard phase (PMMA) material. The coverage by second stage hard phase material is increased by increasing the amount of second stage material, other reaction parameters kept constant. The interface thickness increases with increasing shell content.

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