Film Formation from Dispersion of Core−Shell Latex Particles

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Received June 21, 1994; Revised Manuscript Received December 5, 1994[⊗]

ABSTRACT: Small amounts of organic solvents are often postadded to latex dispersions as aids to promote film formation. However because of their toxicity, the use of these solvents will be prohibited in the near future. An alternative solution to this problem may be the use of new tailored core−shell particles. We have monitored the extent of mixing of the latex particles during film formation using the fluorescent nonradiative energy transfer technique. We report promising results obtained with poly(butyl methacrylate) core−copolymer (butyl methacrylate−butyl acrylate) shell latex particles. We show that films obtained from these dispersions are comparable to those obtained from solvent-added poly(butyl methacrylate) latex dispersions in terms of polymer interdiffusion across particle boundaries.

Introduction

In the process of latex film formation, further gradual coalescence of latex particles is an important step since it mainly determines the mechanical properties of the film. This step is characterized by the diffusion of polymer chains across the particle interfaces in the dry film. Recently,[1] we have studied the effect of organic solvents on the rate of diffusion of polymer chains between adjacent particles. Indeed, organic solvents are often added to latex dispersions as filming aids. Their role is to increase the rate of polymer diffusion by decreasing the glass transition temperature, T_g, of the polymer. This facilitates particle deformation during the last stage of water evaporation and interparticle chain diffusion in the dry film above T_g. Moreover these organic solvents are supposed to evaporate off the film in order to restore to the polymer its mechanical properties. However the use of these organic solvents in latex dispersion is expected to be prohibited in the future for ecological reasons. We show that core−shell particles can mimic the effect of filming aids in film formation in terms of interparticle chain diffusion and can therefore be an alternative solution to the use of organic solvents.

Materials and Methods

Polymer Chain Interparticle Diffusion Measurements. Two methods have been used to study the diffusion of polymer chains between adjacent latex particles at a molecular level. In the first one the increase in size of deuterated particles embedded between hydrogenated particles has been measured, by small angle neutron scattering, as a function of the film annealing time.[2] In the second method one uses the direct nonradiative energy transfer (DET) mechanism[3] which appears between the energy donor and acceptor covalently bonded to the polymer chains when the chains are sufficiently close to each other. The latter method, which has been pioneered by Winnik and co-workers,[4] was used in the present work. It has been described in detail in the literature.[1,4−6] We will only shortly recall the principle of this method.

A film is formed with an equal number of donor and acceptor labeled particles. This film is annealed for a given period of time above T_g, and the fluorescence emission of the donor is recorded, below T_g. A decrease of the donor fluorescence indicates an increase in energy transfer which results from the diffusion of the labeled polymer chains across the interparticle interface. It has been shown[4−6] that, from the analysis of the fluorescence decay curve, one can calculate the volume fraction of mixing f_m of donor and acceptor labeled chains. Using a Fickian model of diffusion, the polymer chain diffusion coefficient, D, and the interparticle distance of penetration d_p (see eq 6 in ref 1) can be determined. In the present work only the variations of f_m and d_p versus annealing time will be given. Recently, it has been shown[7] that the simplified model described above,[4,5] in which acceptor and donor concentration gradients are ignored, yields an underestimated polymer self-diffusion coefficient. However, the conclusion about the relative rate of polymer migration stays valid. Therefore, comparison between the variations of f_m and d_p versus annealing time for the various latexes synthesized for the present study are significant. We will see that, from this comparison, the analogy between the role of a "good" filming aid and the behavior of some adequately tailored core−shell particles, in the process of further gradual coalescence, clearly emerges.

Latex Synthesis. Homogeneous particles made of poly(butyl methacrylate) (PBMA) and core−shell (CS) particles with a poly(butyl methacrylate) core and a copolymer (butyl methacrylate−butyl acrylate) shell have been synthesized by semicontinuous free radical emulsion polymerization using potassium persulfate as the initiator. The synthesis of the homogeneous PBMA latex particles has been made by following the procedure described by Zhao et al.[5] The same procedure has been used for the preparation of the core−shell particles except that at the end of the second step of the reaction butyl methacrylate (BMA) (which is expected to form the core of the particles) was replaced by a mixture of BMA and butyl acrylate (BA) (which is expected to form the shell of the particles).[8] The monomer BA was from Aldrich (99%). The origin of the other compounds is given elsewhere.[1] The composition of the shell copolymer was 80 mol of butyl methacrylate for 20 mol of butyl acrylate, having a T_g of 15 °C according to the Fox law. (9-Phenanthryl)methyl methacrylate was incorporated as a energy donor and 9-anthryl methacrylate as an energy acceptor in the polymer chains during two independent synthesis. The molar concentration ratio [donor or acceptor]/[monomer] was less than 0.01. The Förster radius R_0 is in this case equal to 2.3 nm, which is much smaller than the diameter of the particles (about 130 nm; see Table 1) and ensures an accurate probe of the interdiffusion of the donor and acceptor labeled polymer chains, as the film is annealed for various periods of time. The particle sizes and the molecular weight of the polymers synthesized are given in Table 1.

Concerning the structure of the particles we have checked, using an atomic force microscope (AFM), that the surface of the particles was of a rather spherical shape, as found for instance for PBMA latex particles studied earlier by AFM.[9] No particle with a double hemisphere or with raspberry-like shape, for instance, could be observed on the AFM images. This was an indication for us that regular core−shell particles might have been synthesized, but of course, this was not a real proof of it. It is well-known that direct evidence of the real structure of core−shell particles is very difficult to obtain. Transmission electron microscopy (TEM) gives images which present sometimes a high contrast between the core and the

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[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1995.

0024-9297/95/2228-1306$09.00/0

Table 1. Diameter d of the Latex Particles and Weight Average, M_w, and Number Average, M_n, Molecular Weights of the Polymers Labeled with Phenanthrene (Phe) and Anthracene (An) Fluorescent Probes

		d (nm)	M_w	M_n
PBMA homopolymer	Phe	139	600 000	89 000
	An	148	500 000	44 000
CS1 (shell = 5 nm)	Phe	133	590 000	75 000
	An	123	524 000	72 000
CS2 (shell = 3 nm)	Phe	135	590 000	80 000
	An	125	520 000	70 000

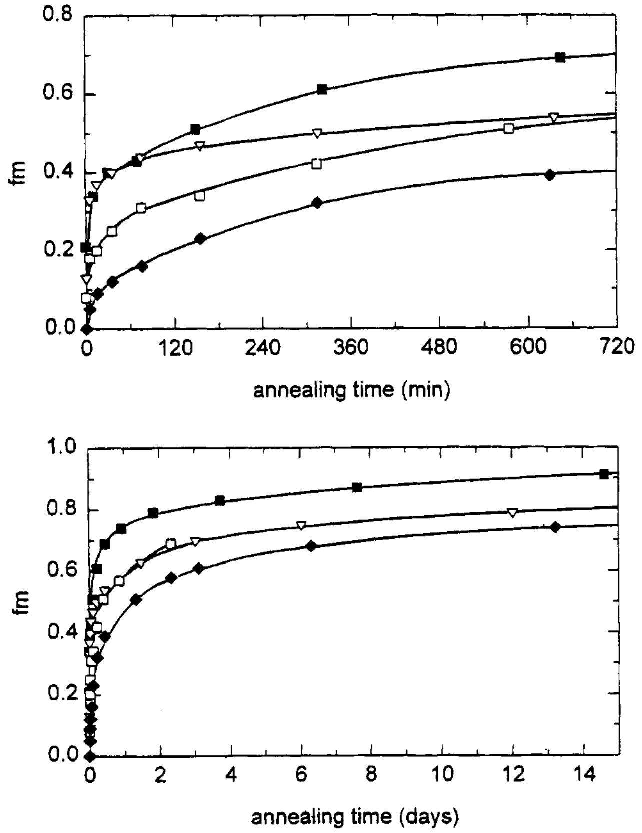

Figure 1. Volume fraction of mixing f_m versus annealing time at 70 °C for the PBMA latex films with no additive (◆) and with DGB (▽) and for the core–shell latex films CS1 (■) and CS2 (□).

shell of the particles.[10] This could be observed for particles with cores and shells of very different chemical natures. In our case, both the core and the shell were made of acrylic polymers, and therefore no direct evidence of the particles structure was expected to be easily found with the TEM method. However, as shown in the following, our fluorescence measurements give indirect evidence that our synthesis has led to the formation of particles with a shell of lower T_g (therefore probably made mainly of BMA–BA copolymers) than the T_g of the core (therefore probably made mainly of PBMA), and thus that the expected core–shell particles have been probably really synthesized.

Film Preparation. Dispersions containing an equal amount of donor-labeled and acceptor-labeled particles were cast on a quartz plate at 23 °C. For the film containing the filming aid diethylene glycol monobutyl ether (DGB) a weighed amount of DGB (10 wt % based on polymer) was first added to the dispersion which was allowed to equilibrate under gentle stirring for 8 days. All films were annealed at 70 °C, i.e. 36 °C above the T_g value of PBMA and also well above the T_g value of the shell in the experiments with CS particles.

Results and Discussion

Figure 1 shows the variations of f_m versus annealing time for four different films. Very striking differences can be seen in these variations. The film made with the homopolymer PBMA in the absence of filming aid presents the lowest values of f_m for a given annealing time. This indicates that in this film, polymer chain migration is slow. Addition of DGB increases considerably the value of f_m for a given annealing time. This result was qualitatively expected for a "good" filming aid whose role is to facilitate the polymer diffusion. Notice that in the presence of DGB a small volume fraction of mixing is already observed in the nascent film. This is due to a plasticizing effect of the particle surface by DGB which produces a small chain interpenetration at the particle surfaces, even before annealing of the film.[1]

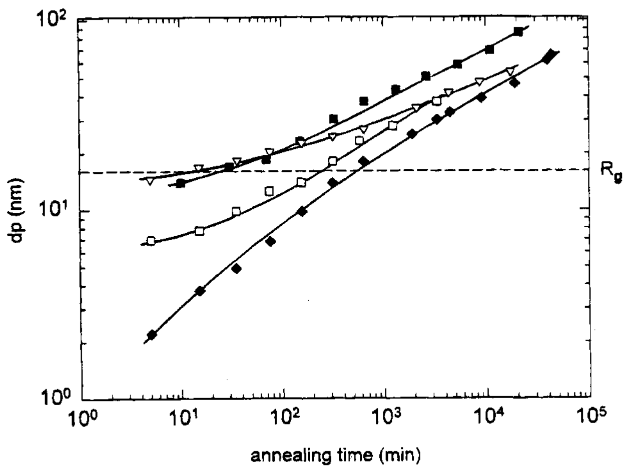

Figure 2. Interparticle penetration distance d_p versus annealing time at 70 °C for the PBMA latex films with no additive (◆) and with DGB (▽) and for the core–shell latex films CS1 (■) and CS2 (□).

The increase in the polymer chain migration induced by DGB is even more apparent in the variations of d_p versus annealing time shown in Figure 2 where the horizontal dashed line represents the polymer radius of gyration, R_g. R_g is an important parameter which helps us to understand the role played by a filming aid in the process of film formation and of film mechanical strength recovery. Indeed, it has been shown theoretically[11] and experimentally[12] that the interface between two polymer surfaces brought into contact is healed, in terms of mechanical resistance, when polymer chains have diffused across the interface over a distance equal to one radius of gyration. Figure 2 shows that the interpenetration distance equals R_g after 600 min of annealing for the PBMA film without DGB whereas in the presence of DGB this time is considerably reduced since it is only equal to 10 min. There is therefore a great advantage in using DGB if one wishes to quickly attain a good mechanical resistance of the film. Another difference appears in the d_p versus annealing time curves. A downward curvature appears for the film containing no additive, and an upward curvature, for the film containing DGB. As a result the curve for the film with DGB tends to become closer and closer to the one without DGB at large annealing times. This has been explained as being due to the fact that at short annealing times DGB greatly plasticizes the particles but, as time goes on, DGB evaporates off the film and the rate of film interpenetration decreases and approaches the rate observed with the films without additive.[1]

If we now turn to the f_m and d_p variations observed for the films formed with the core–shell particles, one can notice analogies and differences of behavior with films obtained with DGB-added homopolymer particles. In Figure 1 one sees that the values of f_m for the films made with core–shell particles are above the values found for the additive-free homopolymer particle films. The rate of interparticle chain migration is therefore larger with the core–shell particles than with the homopolymer particles. Moreover the film made with CS1 behaves similarly to the film containing DGB at short annealing times. There is therefore a great analogy in the variations of f_m for the film made with core–shell particles CS1 and the film made with homogeneous particles containing DGB. However at large annealing times a difference appears between the values of f_m for the CS and DGB-added films, which is discussed below.

The variations of d_p with annealing time reported in Figure 2 show that core–shell particles offer the same advantage as DGB in the sense that the time necessary to reach R_g is much shorter than with the additive-free homopolymer particles. Notice also that for the film with CS1 this time is shorter (24 min) than it is for the film with CS2 (240 min). This is due to the thicker shell of the CS1 particles (estimated to be 5 nm, based on the recipe) compared to the shell thickness of the CS2 particles (estimated to be 3 nm, based on the recipe). Therefore we show here the similarity which exists between the effect of addition of DGB in a latex made of homogeneous particles and of core–shell particles, on the rate of chain migration mainly at short annealing times, which, in practice, is the most important period of time since a quick recovery of the mechanical strength of this film is usually required.

At large annealing times one observes differences in behavior between the DGB-added film and the CS films. Although this difference appears also in the variation of f_m shown in Figure 1 it appears more clearly in the variations of d_p reported in Figure 2. In Figure 2 one sees that for the film containing DGB the curve slowly becomes closer to the additive-free film curve whereas for the CS films a constant difference in the d_p values appears at large annealing times. Since d_p is reported in a log scale in Figure 2 this means that the rate of interpenetration remains faster in the CS film than in the additive-free film even at large annealing times, contrary to what is observed with the DGB-containing film. This difference in behavior between the CS films and the DGB film comes from the fact that DGB evaporates from the film. The T_g of this film becomes therefore slowly equal to the T_g of the additive-free film. In the case of CS particles, in the course of the chain migration, the T_g in the mixing region stays always below the T_g of the homogeneous additive-free particles, since it results from the mixture of the core and the shell, the T_g of the copolymer of the shell being lower than the T_g of the core. The T_g of the final film made originally with the CS particles is, however, only slightly lower than the T_g of the film obtained with the homogeneous PBMA particles. A decrease of 4 °C is obtained for the final film made with CS1 and of 2 °C with the final film made with CS2, compared to the T_g of the film made with PBMA particles ($T_g = 34$ °C). This is due to the small thickness of the shell for the CS particles that have been synthesized. Note that the largest shell thickness has been synthesized for CS1 (5 nm) and represents only 4% of the diameter of the particle and 12% of its weight.

Finally, it seems useful to point out that the present results obtained by DET are as expected for the core–shell particles that we intended to synthesize. Indeed, if in the CS preparation, homogeneous particles, with simply a lower T_g than for homogeneous PBMA latex particles, would have had been synthesized, the d_p versus annealing time curves would have had the same shape, i.e. presenting the same downward curvature, as that for the PBMA particles, with only slightly larger d_p values (lower T_g). Instead, the curves obtained with the CS particles present an upward curvature, which comes from a larger rate of chain migration at short annealing times, therefore concerning the outside first layer (shell) of the particles. Moreover the d_p value increases with the shell thickness. Therefore, although we have no direct evidence of the real structure of our particles, except for the fact that differential scanning calorimetry indicates the existence of two phases in our latex, the present study brings, in terms of film further gradual coalescence, a serious argument in favor of a successful synthesis of our desired core–shell particles.

Conclusion

We showed that tailored core–shell particles can offer the same advantages as homogeneous particles postadded with a filming aid and avoid the disadvantage of solvent emission during the film formation process. When the thickness and the glass transition temperature of the shell are optimized, intrinsic properties of the final film, that is to say that of the core polymer, are not significantly altered. Therefore one has access to a wide range of applications where solvents need to be replaced. We also showed that the DET technique can bring arguments to the expected core–shell structure of latex particles.

Acknowledgment. The authors thank ELF Aquitaine and ELF Atochem for their financial support of this research and their interest in the project.

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MA941256Q