Macromol. Symp. ***151,*** *459–464 (2000)*

The Molar Mass Dependence of Latex Particle Deformation

J. A. M. de Brouwer*, J. J. G. S. van Es, A. L. German

Department of Polymer Chemistry & Coatings Technology,
Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven,
The Netherlands

SUMMARY: As a first step in the study of the molar mass dependence of film formation, the rate of deformation and the spreading of individually adsorbed latex particles has been measured under dry conditions using atomic force microscopy. These data recorded at different temperatures and for particles with different molecular weights have been compared with glass transition temperatures and minimum film formation temperatures. The preliminary results indicate that the speed of the deformation process depends on both molar mass and temperature, while the maximum extend of spreading only shows a molar mass dependence close to Tg.

Introduction

Polymeric binder systems for coating applications have to meet conflicting demands. On one hand, polymer molar mass should be low to allow film formation to occur at an appreciable rate and a homogeneous film to be created. On the other hand, mechanical properties of the resulting coating layer are strongly dependent on polymer molecular mass and in this case a higher molar mass results in better performance. Many low cost latices settle for a compromise at an intermediate molar mass, or make use of plasticizers, compounds undesirable from an environmental point of view. In our laboratory a method has been developed to prepare low molecular weight telechelic latices1). The low molecular weight ensures a proper film formation while the functional chain-ends allow the mechanical properties to be build up through chain extension reactions or network formation. It is of paramount importance for the quality of the resulting coating that the rates at which film formation and crosslinking take place are adequately balanced. In this publication we would like to report some preliminary results on the molar mass dependence of film formation.

CCC 1022-1360/00/$ 17.50+.50/0

Theory

The film formation process of a latex binder is usually divided in several steps with coalescence of the particles following a flocculation phase[2)]. After these steps, the particles are closely packed together and deformed by the pressure laid upon them by capillary forces. Finally, the autohesion process where polymer diffuses across the original particle boundaries has to provide the film with its required strength. A lower molecular weight, resulting in a lower polymer viscosity, will make the latex particles more susceptible to deformation during the coalescence phase, but most performance can be gained during the autohesion phase where increased polymer diffusion is expected to improve tremendously film homogeneity. The maximum obtainable film strength will be less as compared to that of high molecular weight polymer but the rate at which this strength builds up will be much higher. After film formation, functional groups attached to the polymer chain-ends will through crosslinking reactions ensure outstanding film properties. We presume that the ideal molar mass is found just below the entanglement limit. At this point, polymer mobility is relatively high, while only a minimum amount of crosslinking is required afterwards to raise the molecular weight sufficiently to a regime that exhibits the better mechanical properties.

Several experiments have been performed to examine polymer mobility as a function of molar mass. Poly(*iso*-butyl methacrylate) (PiBMA) was chosen as the model polymer for these studies as its glass transition temperature (Tg) proved to be sufficiently high to prevent undesired particle deformation during handling at room temperature.

Experimental

The PiBMA latices of the present investigation were prepared by a surfactant-free batch emulsion polymerization. In a typical preparation, 24 ml of *iso*-butyl methacrylate monomer (Aldrich) and 0.09 g of potassium persulfate (Merck, 99%) were added to 150 ml of water in a double-wall jacketed glass reactor equipped with a mechanical stirrer, condenser, and argon gas inlet. Polymerization was carried out under argon at 80°C and reached high conversions within six hours. The molecular weight of the various samples was controlled by the addition of *tert*-dodecylmercaptan (Fluka, 95%) as a chain transfer agent. The mixture of *tert*-dodecylmercaptan and *iso*-butyl methacrylate was added to the water while stirring. Polymerization was started by the addition of potassium persulfate, dissolved in water. Both monomer and water were purged with argon before use. A total of 13 PiBMA latices were prepared with different molecular weights, while other latex characteristics were kept constant. All latices were thoroughly dialyzed before use.

The weight average molar mass of the latices used, ranged from $3•10^4$ to $7•10^5$ g/mol. Polydispersity indices were similar for all latices and had a value of around 3.5. The particle diameter was measured with Dynamic Light Scattering (Autosizer 2c, Malvern Instruments Ltd., England). For all latices the average diameter fell into the range of 430 ±25 nm.

The ζ-potential of the latices was determined using a Zetasiser 3, Malvern Instruments Inc., England. For all latices the ζ-potential was -55 ±4 mV.

The Tg's of the latices were determined by Differential Scanning Calorimetry (DSC 7, Perkin Elmer, Netherlands). The Tg was determined at a temperature scan rate of 10°C/min.

Minimum film formation temperature (MFFT) measurements were performed on an MFFT-bar (SS-3000 SHEEN). The latices were applied on the bar and film formation was allowed to proceed at different temperature gradients. The drying latices were subjected to a stream of dry nitrogen at a flow of 4.7 dm^3/min.

AFM samples of individually adsorbed latex particles were prepared similar to a procedure reported in litterature3). The surface of freshly cleaved muscovite mica was treated for three hours in a buffered solution ($NaHCO_3/Na_2CO_3$, pH 9.9) of branched poly(ethyleneimine) (PEI, Aldrich, $Mn=8\cdot10^4$ g/mol). This surface modification was applied to allow adsorption of the particles with a negative surface potential onto the substrate surface. The mica was thoroughly rinsed with water immediately before use. Samples of individually adsorbed particles were prepared by adsorption from a diluted latex (volume fraction particles $\phi=1•10^{-4}$) at an ionic strength of 0.025 mM ($NaHCO_3$) for 90 minutes. Agglomerates of particles were obtained at ionic strengths of 0.1 to 0.4 mM in combination with longer adsorption times.

After adsorption the mica sheets were withdrawn from the suspension and non-adsorbed latex particles were removed by immersion of the mica in deionized water. Excess water was removed by carefully contacting the side of the mica sheet with a piece of filtration paper, and the sample was dried at 4°C to prevent premature deformation of the latex particles. AFM images were obtained randomly on the mica surface, in tapping mode. The height of at least 50 particles was determined for every sample.

Glass Transition & Film Formation Temperatures

Both the Tg and the MFFT showed a similar dependency on molar mass (Fig. 1 & 2). This dependency is very strong in the low molecular weight region up to a number average molar mass of $5•10^4$ g/mol. Above this value a plateau is reached where Tg and MFFT become virtually independent of molar mass. The molar mass that corresponds to this transition marks

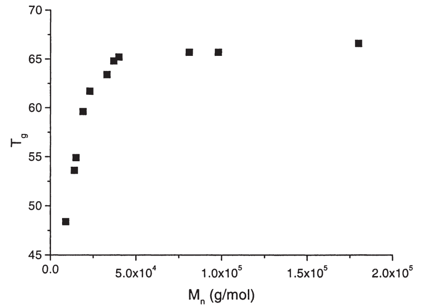

Fig.1: Tg of poly(iso-butylmethacrylate) as a function of molar mass. (polydispersity indices≈3.5)

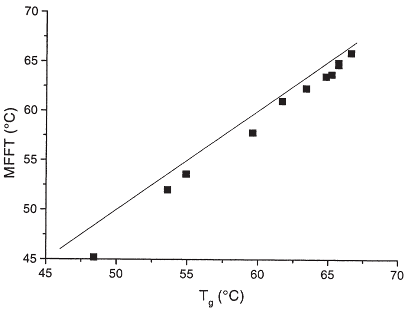

Fig.2: Correlation between the Tg and the MFFT for the corresponding latices(■). The line denotes the situation where Tg equals MFFT.

the point where entanglement coupling starts to dominate the polymer viscoelastic properties. Literature$^{4)}$ reports values of $2 \cdot 10^4$ g/mol for the apparent molar mass between two entanglements (M_e). The critical molar mass (M_c) where entanglement coupling starts to take place is twice to three times M_e and coincides with the onset of the plateau that was found in these Tg measurements.

The MFFT shows a similar trend, though its values are somewhat lower than the Tg. The difference becoming larger at lower molecular weight. We attribute this fact to the plasticizing effect of water which becomes slightly more soluble in the polymer at lower molecular weights.

Atomic Force Microscopy

Before studying the coalescence of particles and actual film formation, the deformation behavior of individual particles was examined in order to separate phenomena originating from interparticle interactions from those inherent to individual particles. Three latices were selected for AFM measurements (table 1).

Table 1. Data of PiBMA latices that were used for AFM measurements.

Latex	M_n (g/mol)	Tg(°C)	MFFT (°C)	$(h/h_0)_{min,70°C}$	$(h/h_0)_{min,79°C}$
1	$1.1 \cdot 10^5$	65.7	64.9	0.48	0.18
2	$3.2 \cdot 10^4$	64.8	61.5	0.31	0.19
3	$1.2 \cdot 10^4$	48.4	45.1	0.19	0.16

When adsorption took place from solutions with ionic strengths in the range of 0.1 to 0.4 mM, agglomerates of particles were formed. These showed a regular packing over larger distances, confirming the monodisperity of the particle size distribution. Adsorption at an ionic strength of 0.025 mM for 90 minutes rendered the desired isolated particles on the substrate. The poly(ethyleneimine) layer successfully keeps the particles in place and prevents particle clustering by the lateral capillary forces during drying, which is sometimes observed when samples are dried below their Tg[5,6)]. Analysis of the samples before annealing showed that the latex particles are essentially undeformed. The average particle height showed no structural deviation from the diameter determined with DLS.

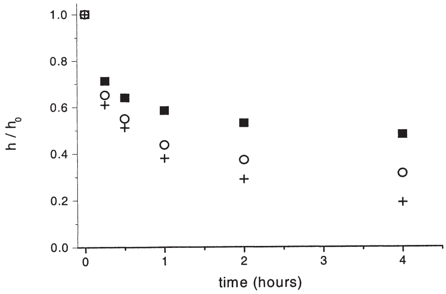

Fig. 3: Decay of relative particle height at 70°C; ■ latex 1,○ latex 2,✚ latex 3.

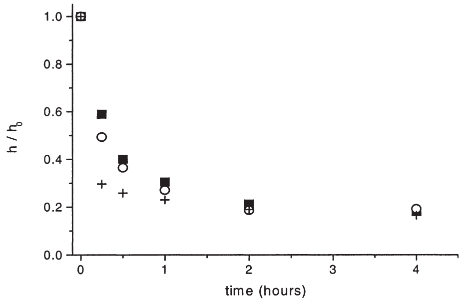

Fig. 4: Decay of relative particle height at 79°C; ■ latex 1,○ latex 2,✚ latex 3.

The particle height was then recorded as a function of annealing time at a specific temperature (fig. 3 & 4). During annealing the particles spread on the substrate surface and their height decreased. Interfacial tension is the driving force governing this process, while the rate at which deformation takes places is dictated by the polymer viscoelastic properties[5)]. Based on the similarities of the particle sizes and surface charges of the latices, the driving force for deformation is expected to be the same for all latices at a set temperature[6)]. Surface tension does exhibit a molar mass dependence, but data of similar polymers show that over this range of molecular weights the change in surface tension is only a few percent[7)].

After annealing for 4 hours at 70°C the particles were spread to their maximum extend (fig. 3), indicating that the surface forces had reached equilibrium. Longer annealing times had no significant influence on the particle height. It is remarkable to note that the three latices reach different levels of spreading. The large differences in spreading are most likely due to the change in temperature dependence of the surface tension around Tg, combined with the broad molecular weight distribution. This explanation is supported by the fact that at 79°C (fig. 4) and 91°C all latices reach the same level of spreading.

Figures 3 and 4 also show the influence of the polymer molar mass on the speed of the deformation process. As expected, higher temperatures and lower molecular weights exhibit faster deformation. The similarity of latex 1 and 2 in terms of Tg is not reflected in the rate of spreading.

Currently these data are being compared with the decay of the corrugation height in complete films to monitor the influence of neighboring particles and allow comparison with data reported in literature[8,9,10)]. Furthermore dynamical mechanical analysis of the annealed bulk polymer is being performed. Integrated results will be published in the near future.

Conclusions

It was found that below an average molar mass of around $2.5 \bullet 10^4$ g/mol mobility of PiBMA chains was greatly enhanced, compared with higher molecular weight polymers. Both Tg and MFFT decreased significantly. It was shown that rate of particle spreading depends on the polymeric chain mobility. The maximum extend of spreading is influenced by the polymer molecular weight at temperatures close to Tg, but at higher temperatures this influence dissapears.

References

1) A difunctional addition-fragmentation chain transfer agent is applied in combination with a functional initiator. See e.g. G. F. Meijs, T. C. Morton, E. Rizzardo, S. H. Thang, *Macromolecules* **24**, 3689 (1991)
2) E.g., J. W. Vanderhoff, E. B. Bradford, W. K. Carrington, *J. Polym. Sci., Polym. Symp.* **41**, 155 (1973)
3) C. A. Johnson, Adsorption behaviour of proteins and coloidal particles studied using atomic force microscopy, 1st ed., 1997, p52-89
4) J. D. Ferry, Viscoelastic properties of polymers, 3th ed., 1980, p374
5) H. Butt, B. Gerharz, *Langmuir* **11**, 4735 (1995)
6) V.Granier, A. Sartre, *Langmuir* **11**, 2179 (1995)
7) S. Wu, Polymer interface and adhesion, 1982, p. 72
8) F. Lin, D. J. Meier, *Langmuir* **11**, 2726 (1995)
9) F. Lin, D. J. Meier, *Langmuir* **12**, 2774 (1996)
10) E. Pérez, J. Lang, *Macromolecules* **32**, 1626 (1999)