Macromol. Symp. **2006**, 243, 63–71 DOI: 10.1002/masy.200651107

Modelling of The Rheological Properties of Bimodal Emulsions

Malihe Pishvaei,[1,2] *Philippe Cassagnau,*[1] *Timothy F. McKenna**[2]

The model of Ouchiyama and Tanaka[1–3] was successfully adapted to calculate the maximum packing fraction (ϕ_m) of polymer latexes with varying bimodal particle size distributions based upon rheological measurements performed on its constituent parts. The values of ϕ_m calculated from the model can be used to predict the rheological properties of the latices. The model was experimentally validated and used for the prediction the viscosity of studied bimodal latices of known concentration using the master curve of viscosity-reduced volume fraction (η vs. ϕ/ϕ_m).

Keywords: bimodal latex; maximum packing fraction; model; rheology; viscosity

Introduction

A series of recent papers on high solid content latices[4–6] reveals the general level of interest in bimodal polymer emulsions. However, it has been clearly pointed out that it is important for the process engineer to be able to predict the viscosity of polymer latices (zero shear and shear viscosities) à priori as a function of the particle size distribution (PSD) and polymer concentration – a task which until now has been difficult to achieve.[5]

The viscosity of a diluted dispersion of non-interacting, monodispersed, undeformable (i.e. hard sphere) particle dispersions is essentially a function of three main parameters: the total volume fraction of particles (ϕ); the viscosity of the continuous phase η_s; and its intrinsic viscosity [η]. In such systems, the maximum packing fraction of particles (ϕ_m) is calculated as a function of the type of packing (e.g. cubic face centred, random…) independently of the particle size. Note ϕ_m for defined system can depend on the applied shear rate. In the low shear limit, typical values for $\phi_{m,0}$ have been found to be near to random close packing ($\phi_m = 64\%$), and about the value of closest packing (74%) for high-shear-limit.[7,8] With this in mind, we will first concentrate on the low shear limit. The high shear viscosity of complex latexes will be treated in a forthcoming article.

This said, polymeric emulsions are not ideal hard sphere systems, so the value ϕ_m of a latex will also depend not only on the PSD, but also on second order effects like particle- particle interactions, and the thickness and composition of the stabilisation layer.[9–11] If one considers the particular case of a bimodal latex, then at a fixed total volume fraction of polymer (ϕ), the rheology will be influenced by the PSD, and in particular by the ratio of the diameter of the large particles to that of the small ones ($\lambda = d_l/d_s$), as well as the volume fractions of these populations ($\zeta = \phi_1/\phi_s$). It should also be clear that the amount of surfactant around the particles will influence the PSD to the extent that the thickness of the stabilisation layer will increase the effective volume fraction of the particles. This will be even more pronounced for smaller particles than for larger ones.[4,12] From the point of view of the viscosity, it is well accepted that the particle size distribution (PSD) that gives the highest maximum packing fraction ϕ_m, will also gives the lowest viscosity for a fixed solid content ϕ[12,13] If we know the shear dependence of the maximum packing fraction, the ϕ- dependence of the

---

[1] LMPB-CNRS/UCBL-Lyon 1, Villeurbanne, France
[2] LCPP-CNRS/ESCPE-Lyon, Villeurbanne, France
E-mail: mckenna@cpe.fr

zero shear viscosity (η_0) and high shear viscosity (η_∞) can be described by the Krieger-Dougherty equation:[14–17]

$$\eta_0 = \eta_s \left(1 - \frac{\phi}{\phi_{m,0}}\right)^{-[\eta]\phi_{m,0}} \tag{1}$$

$$\eta_\infty = \eta_s \left(1 - \frac{\phi}{\phi_{m,\infty}}\right)^{-[\eta]\phi_{m,\infty}} \tag{2}$$

Where η_s is the viscosity of dispersing medium and $[\eta]$ is the intrinsic viscosity.

It should be clear from this (admittedly limited discussion) that phenomenological models can be used to predict the viscosity behaviour of concentrated suspensions – but only if we have data from a given system to fit model parameters. This is not a major obstacle for the case of monodisperse systems. However, systematic studies on rheological behaviour of well-characterised polydisperse dispersions are not so extensive and, up to now, there is not a unique empirical or theoretical model to account for the different variables on flow behaviour of latices having a polydisperse size distribution (PSD).

To over come this limitation, we have adapted the model that Ouchiyama and Tanaka [1–3] proposed to estimate the porosity of a bed of randomly distributed spherical particles with a polydispersed PSD to calculate ϕ_m for a bimodal latex with any combination of particle sizes.

Experimental

Monodisperse latices of polystyrene with different particle diameter of 79, 452, 63, 274 nanometers (referred as M_{79}, M_{452}, M_{63} and M_{274}) were prepared by semibatch emulsion polymerisation using ammonium persulphate (APS) as the free radical initiator.[11] In all of the syntheses, a mixture of anionic (SDS) and steric stabilisers was used. In the preparation of the small particles (M_{63}&M_{79}), Disponil R 3065 (mixture of linear ethoxylated fatty acids) was used as the steric surfactant. In the cases of M_{452} and M_{274}, Triton 405X has been used as non-ionic surfactant. We tried to produce the different monodisperse latices with the same particle surface charge, the intent being to isolate the effect of the particle size on the rheological behaviour of latex. The characteristics of the different emulsions are given in Table 1.

Samples with different polymer concentrations were prepared either by dilution with different amount of water, or by concentration the original latices using vacuum distillation. No salt was added for the preparation of this series.

The average particle size was determined by quasi elastic light scattering (L_0-C from Malvern Instruments, Villeurbanne, France). A polydispersity index (PDI) is provided by the software, which, according to the manufacturers, indicates that the latices are effectively monodisperse if the PDI < 0.1, which is the case here (c.f. Table 1).

All bimodal latices were prepared by mixing monodisperse latexes of different particle sizes in controlled proportions. The composition of the different blends (in terms of volume fraction ratio, $\zeta = \phi_l/\phi_s$) considered here is presented in Table 1. For

Table 1.
Different characters of experimental systems.

Sample name	d (nm) or Volume ratio(ζ)	PDI	ϕ_c(%)	$[\eta]$	ϕ_m(%) by model
M_{79}	79	0.035	45.6	5.5	–
M_{452}	452	0.09	58.5	3.6	–
$B_{452,79,2}$	Bimodal($\zeta = 2$)	–	61.25	4.2	60.58
$B_{452,79,4}$	Bimodal($\zeta = 4$)	–	64.9	4	65.12
M_{63}	63	0.064	45	6.5	–
M_{274}	274	0.029	52.8	4.5	–
$B_{274,63,3}$	Bimodal($\zeta = 3$)	–	58.86	5	59.01
$B_{274,63,9}$	Bimodal($\zeta = 9$)	–	60.5	4.7	61.88

example, the blend of M_{452} and M_{79} with a value of ζ equal to 2 is referred to as $B_{452,79,2}$ (M = monomodal, B = bimodal), and it contains volume fractions of 66.7% for M_{452} and 33.3% for M_{79}. Similarly, $B_{452,79,4}$ contains 80% of volume fraction of M_{452} and 20% of M_{79}. The monomodal styrene latices M_{274} and M_{63} were used to prepare the bimodal latex $B_{274,63,3}$ and $B_{274,63,9}$.

Steady shear viscosity and frequency sweep curves were obtained using a controlled strain Couette rheometer with an inner diameter of 32 mm, an outer diameter of 34 mm, and a cylinder length of 34 mm. All measurements were conducted at ambient temperature (23–25 °C), and the samples were covered with a thin layer of an organic oil to prevent evaporation of water.

Results and Discussion

Viscosity of Monomodal Latices

In many studies the models described by Quemada,[18] and/or by Krieger and Dougherty[14] were used to determine ϕ_m by an extrapolation of viscosity curves.[19, 20] In the work presented here we preferred to approximate ϕ_m by the critical volume concentration, ϕ_c, which is the point where a Newtonian plateau is no longer observed in the viscosity-shear curves. For instance, the variation of the absolute dynamic shear viscosity is shown as a function of the frequency and different volume fraction for M_{79} and M_{452} in Figure 1 and for two bimodal latices ($B_{452,79,2}$ and $B_{452,79,4}$) in Figure 2. The general trends are similar for both monomodal and bimodal latices. In the diluted regime (low total ϕ), the viscosity is nearly constant (i.e. Newtonian behaviour), and only slightly higher than that of the solvent (water). At higher values of ϕ the latices show a pronounced shear thinning behaviour. Finally, as expected, the latices made of larger monomodal particles are significantly less viscous than those composed of smaller ones.

The concentration above which the zero shear Newtonian plateau of viscosity is no longer observed is defined as the critical volume fraction (ϕ_c). The critical packing fraction (ϕ_c) can be used to approximate the maximum packing fraction at low shear limits ($\phi_{m,0}$). Other critical or maximum packing fractions with higher values could be also be found under different conditions. For instance one could consider the absolute maximum packing fraction, $\phi_{m,\infty}$ as the particle volume fraction where the high shear viscosity (high shear Newtonian plateau in the viscosity curves) tends to infinity as an upper limit to the maximum packing fraction. The critical volume fractions ($\phi_c \equiv \phi_{m,0}$) were determined for both mono-modal and bimodal samples and the values are presented in Table 1. Note that it is likely that the values reported in this table are, to a certain extent, a function of both the range of solid content studied (e.g. in the case of M_{452} (Figure 1b), it is possible that the value lie between 57.7 and 58.7), or on the range of frequencies used for the viscosity measurements (e.g. going to even lower values of frequency for M_{79} might lead to a higher value of ϕ_c, closer to 46% than 45.6%). While it is believed that the variations caused by these factors will not be large in the context of this work, it is possible that by refining the measurements even further, we could improve the quality of the master curves obtained for the different products (c.f. Figure 6 below).

The variation of the absolute relative zero shear viscosity ($\eta_{0,r} = |\eta_0^*|/\eta_s$) versus volume fractions for monomodal latices M_{79} and M_{452} is shown in Figure 3. In this Figure, the solid lines represent the Krieger-Dougherty equation using the experimental value of ϕ_c and treating $[\eta]$ as an adjustable parameter (c.f. Table 1). It should be pointed out that the values of η_0 in steady shear condition are equal to the values of the dynamic shear viscosity at low frequency limits (η_4^*). This means that in our experimental systems, the zero shear viscosity of samples obeys the Cox-Merz rule.[11]

All concentrated latices (i.e. with ϕ greater than 35–40%, depending on the system) are non-Newtonian and show shear thinning at a characteristic shear rate ($\dot{\gamma}_c$)

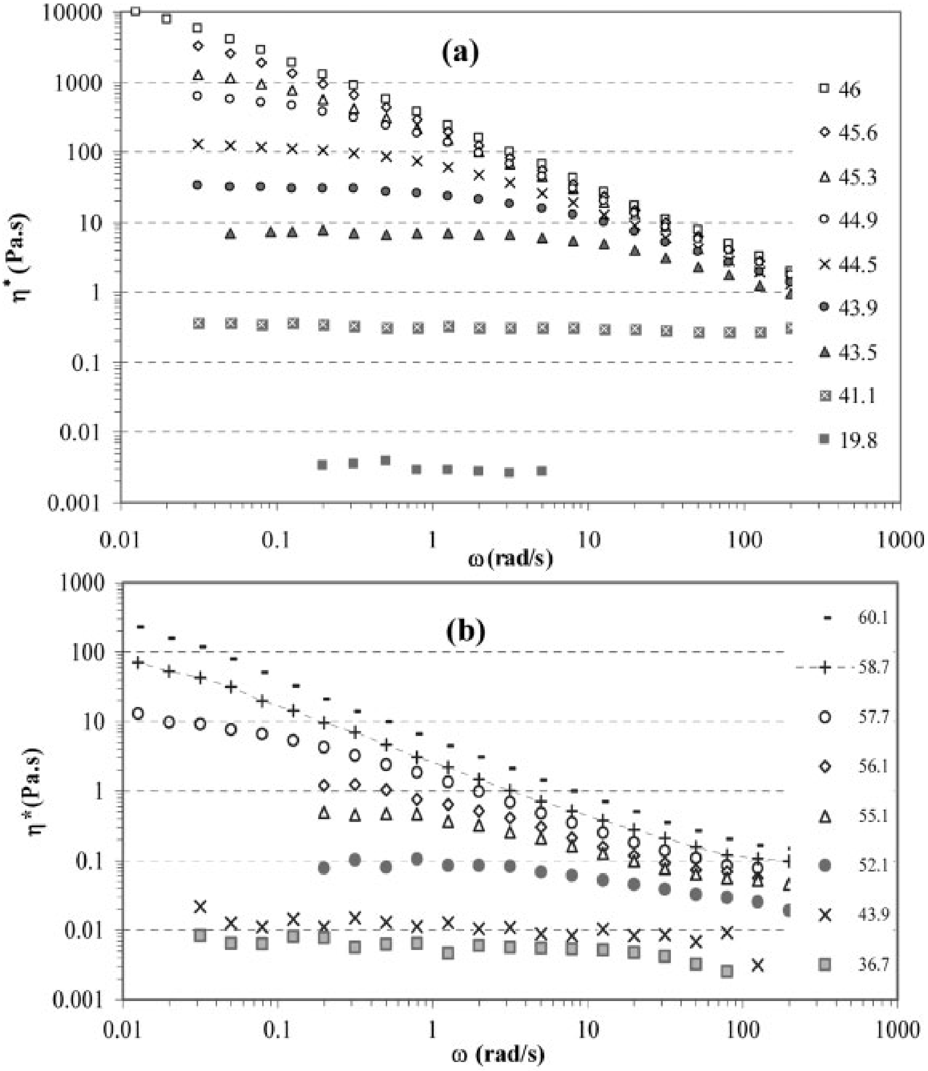

Figure 1.

Variation of the dynamic shear viscosity versus frequency for monomodal latex. The different values of ϕ(%) are presented in the curves. (a) M_{79}; (b) M_{452}.

that depends on the particle size and particle size distribution (PSD). It has been demonstrated that the shear rate characterising shear thinning ($\dot{\gamma}_c$) is the shear rate required for the viscosity to decrease to a halfway between the limiting low and high shear rate viscosities, η_0 and η_∞ respectively.[21,22] We estimated these values by the best fit of the curve of η as a function of $\dot{\gamma}$ By analogy with the behaviour of the zero shear viscosity versus volume fraction of particles, it can be expected that $\dot{\gamma}_c$ can be expressed in the same way as the zero shear viscosity (η_0). Thus we employed the Krieger-Dougherty equation to model the relaxation time (inverse of $\dot{\gamma}_c$) and used the related value of $\phi_{m,0}$ for each series of monomodal samples. τ_s is the relaxation time for continuous medium (water) and $[\eta]_\tau$ is by analogy the intrinsic viscosity for

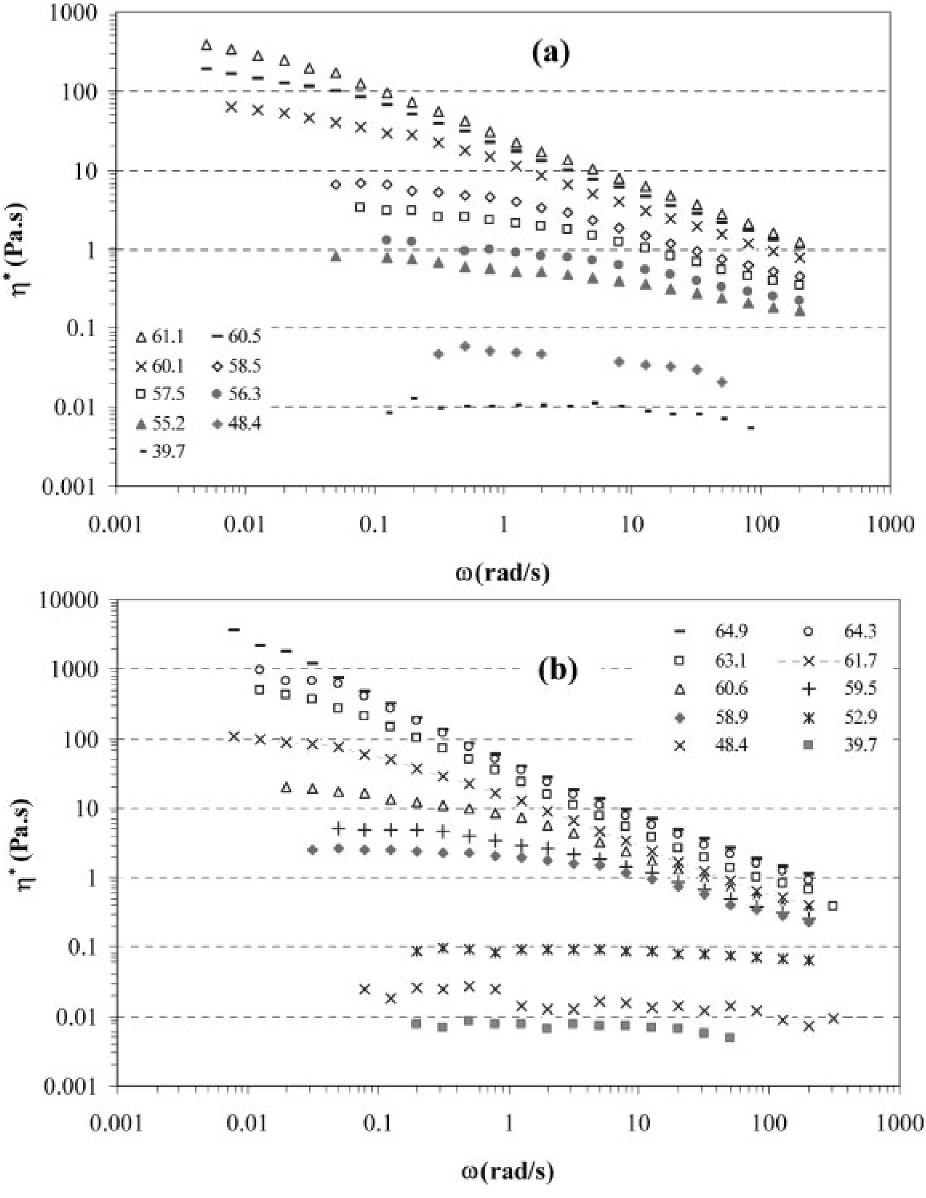

Figure 2.
Variation of the dynamic shear viscosity versus frequency for bimodal latex at different volume fractions. (a) $B_{452,79,2}$; (b) $B_{452,79,4}$.

the shear rate of the onset of shear thinning as follows:

$$\tau = \tau_s \left(1 - \frac{\phi}{\phi_{m,0}}\right)^{-[\eta]_\tau \phi_{m,0}} \tag{3}$$

Surprisingly, fitting this equation with the estimated values of τ, it can be seen in Figure 4 that we find a unique value for τ_s equal to 10^{-4} s, and a unique value for $[\eta]_\tau$ equal to 7 for all samples (including the bimodal samples).

Equations (1) and (2) suggest that both η_0 and η_∞ depend on volume fraction of polymer as described by the Krieger-Dougherty equation. The results in

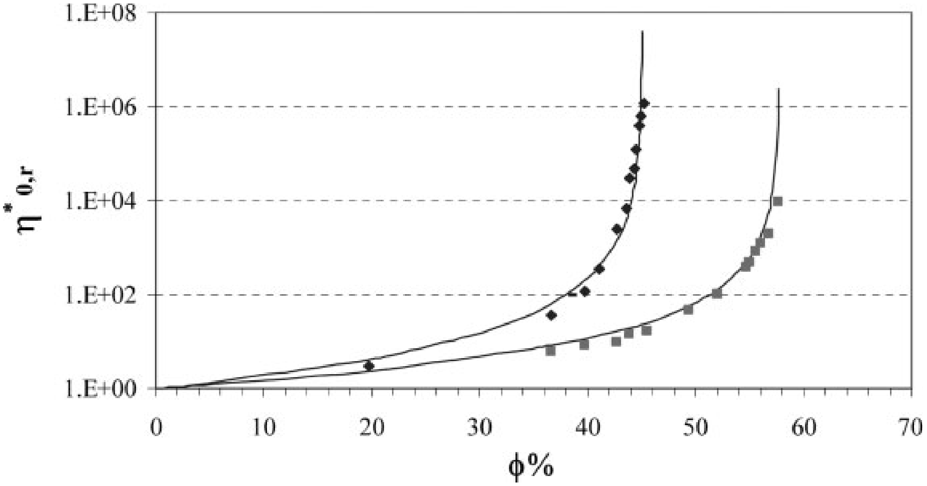

Figure 3.
Variation of the relative zero shear viscosity versus volume fractions for M$_{79}$(◆) and M$_{452}$(■); solid lines the curves according to Krieger-Dougherty equation using the data of Table 1.

Figure 5 show that this is indeed the case for the products treated here, and that as expected,[23,24] $\phi_{m,\infty} > \phi_{m,0}$. In addition the intrinsic viscosity at high shear, $[\eta]_\infty$, is close to the asymptotic value $[\eta] = 2.5$ for rigid spheres without electrosteric interactions.

Viscosity of Bimodal Latices

The models proposed by Farris[25] and Sudduth [26–28] are starting points for more recent equations for predicting the viscosity in multimodal systems. However, Farris' model does not account for interactions between the particles, and has been shown

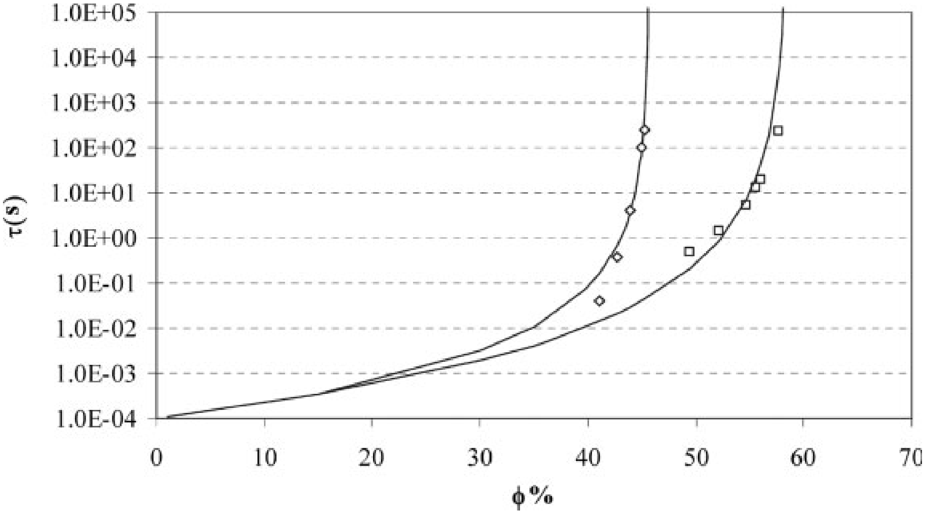

Figure 4.
Variation of the relaxation time versus volume fractions for monomodal latexes M$_{79}$ (◇) and M$_{452}$(□). The solid curve is the predictions of the Krieger-Dougherty equation.

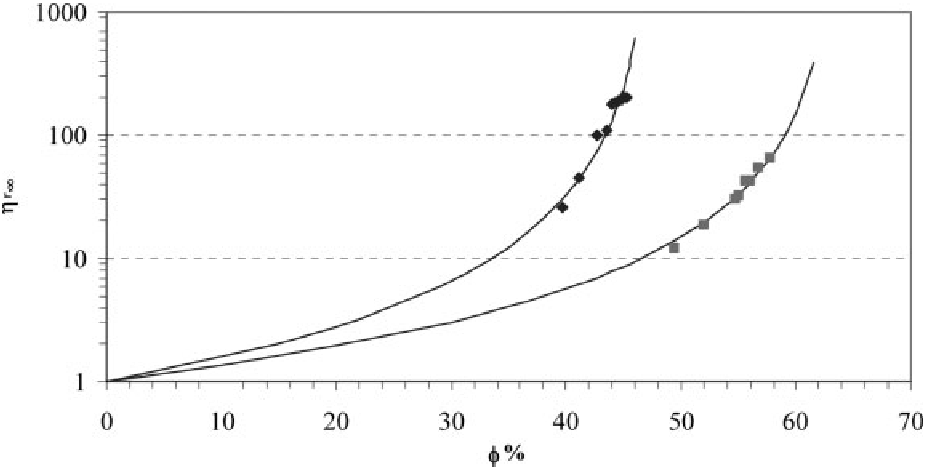

Figure 5.
Variation of the relative high shear viscosity versus volume fractions of monomodal M_{79}(◆) and M_{452}(■) latices. The solid lines are the Krieger-Dougherty equation.

to fail in the case of typical colloidal dispersions.[21] In the model proposed by Sudduth, the viscosity of multimodal system is calculated based on several parameters such as $[\eta]$, and ϕ_m, in a manner similar to the Krieger-Dougherty model. However there are two additional quantities included in this model: the particle interaction coefficient and the width of the PSD. While this model shows some promise to the extent that it is perhaps one of the first practical works to allow us to explicitly introduce the PSD on the calculation of the viscosity, it still includes a number of parameters that have be fit *à posteriori*.

As mentioned above, we have adapted the discrete form of the model proposed by Ouchiyama and Tanaka[1–3] to predict the maximum packing fraction for different bimodal polymeric lattices. The values of ϕ_m calculated from the model will be used to predict the rheological properties of the latices and the resulting previsions will be experimentally validated. It should be kept in mind that this approach requires some *à posteriori* fitting – but only of parameters related to monomodal latexes. Once this information is available, we can fit the viscosity data for bimodal systems with any PSD. This approach is first developed for the zero shear viscosity of bimodal latices then extended to help calculate the other parameters of Yasuda-Carreau law ($\varepsilon = \eta_{\infty:}, \tau$) through the calculation of their respective maximum packing fraction $\phi_{m,\varepsilon}$ using equation (4):

$$\phi_m = \frac{\sum_{i=1}^{2} D_i^3 f_i}{\sum_{i=1}^{2} (D_i \approx \overline{D})^3 f_i + \frac{1}{\overline{n}} \sum_{i=1}^{2} [(D_i + \overline{D})^3 - (D_i \approx \overline{D})^3] f_i} \tag{4}$$

where

$$\overline{n} = 1 + \frac{4}{13} \overline{D} \times \frac{\sum_{i=1}^{2} (8\phi_i^m - 1)(D_i + \overline{D})^2 \left(1 - \frac{3}{8} \frac{\overline{D}}{D_i + \overline{D}}\right) f_i}{\sum_{i=1}^{2} [D_i^3 - (D_i \approx \overline{D})^3] f_i}$$

In this equation, D_i is the diameter of the spheres of population *i*, f_i is the number fraction of the i^{th} component constituting the suspension, $\overline{D} = \sum_{i=1}^{m} D_i f_i$, and$\phi_i^{m,\varepsilon}$ is the maximum packing value observed in the uniform sized spheres system.[1–3] The model predictions for the bimodal systems are in good agreement with values of ϕ_c measured for the blends $B_{452,79}$ and $B_{452,79,4}$ (c.f. Table 1 where the calculated values of ϕ_m are also reported).

Some authors obtained the master curves for both mono- and bimodal hard

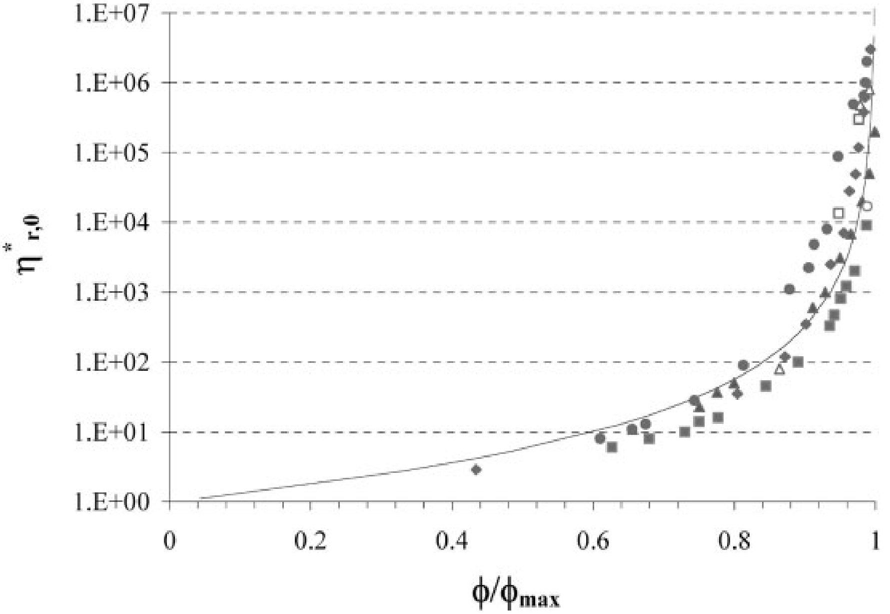

Figure 6.
Master curve of relative zero shear viscosity as a function of excluded volume fraction of particles for monomodal samples of M79(◆), M452(■), M274(△) and bimodal samples of B452,79,2(▲), B452,79,4(●), B274,63,9(□), B274,63,3(o); solid line: the curve according to Krieger-Dougherty equation with $[\eta] = 5.5$.

sphere dispersions when the relative zero shear viscosity is plotted versus the rescaled volume fraction ϕ/ϕ_m.[21,29,30] Such a curve is shown in Figure 6 where we see the variation of $\eta_{0,r}$ as a function of ϕ/ϕ_m, where ϕ_m is calculated from our model separately for each latex (or the measured value used in the case of the monomodal latices). The effect of particle size on the zero shear viscosity of monodisperse latices and the effect of bimodality of dispersed particles can also be seen in this Figure. Finally, for any bimodal, or more generally a multimodal latex, ϕ_m can be estimated from the presented model and then the viscosity can be predicted at any solid content from the master curve.

Conclusion

In this work we presented the study of the rheological behaviour of model latices composed of polystyrene spheres. The main objective was to predict the complex rheological behaviour of these concentrated latices at low shear. For this purpose, bimodal latices were prepared from mixtures of monomodal products. The rheological behaviour of both types of latices was characterized. Subsequently, the expression proposed by Ouchiyama and Tanaka was successfully developed to calculate the maximum packing fraction of a bimodal dispersion from rheological measurements performed on its constituent parts. This shows that the complex viscosity behaviour of concentrated bi-modal latices can be predicted from the rheological behaviour of monomodal ones. In addition, the prediction the viscosity of studied bimodal latices of known concentration can be performed using the master curve of viscosity-reduced volume fraction (η vs. ϕ/ϕ_m).

Finally, this phenomenological approach shows that the complex rheological behaviour of polydisperse latices can be predicted if we only know the rheological behaviour of the corresponding monomodal latices. Work in course will demonstrate that this approach can be extended to the modelling of the dynamic rheological properties of a latex with any PSD.

[1] N. Ouchiyama, T. Tanaka, *Ind. Eng. Chem. Fundam.*, **1981**, *20*, 66.

[2] N. Ouchiyama, T. Tanaka, *Ind. Eng. Chem. Fundam.*, **1984**, *23*, 490.

[3] N. Ouchiyama, T. Tanaka, *Ind. Eng. Chem. Fundam.*, **1986**, *25*, 125.

[4] S. Boutti, C. Graillat, T. F. L. McKenna, *Polymer*, **2005**, *46*, 1189.

[5] M. M. do Amaral, **2003**, Industrial aspects of miniemulsion polymerisation. PhD thesis, University of Basque Country, San Sebastian, Spain.

[6] A. Guyot, F. Chu, M. Schneider, C. Graillat, T. F. L. McKenna, *Prog. Polym. Sci.*, **2002**, *27*, 1573.

[7] J. Bicerano, J. F. Douglas, A.B. Douglas, J. M. S.- Rev. *Macromol.Chem.Phys.* **1999**, *C39*, 561.

[8] W. E. Smith, C. F. Zukoski, *J. Rheol.*, **2004**, *48*, 1375.

[9] R. L. Hoffman, *J. Rheology*, **1992**, *36*, 947.

[10] F. M. Horn, W. Richtering, *J. Rheol.*, **2000**, *44*, 1279.

[11] M. Pishvaei, C. Graillat, T. F. McKenna, P. Cassagnau, *Polymer*, **2005**, *46*, 1235.

[12] R. Greenwood, P. F. Luckham, T. Gregory, *J. Coll. Interfac. Sci.*, **1997**, *191*, 11.

[13] R. Greenwood, P. F. Luckham, T. Gregory, *Coll. Surf., A: Physicochem. Eng Aspects*, **1998**, *144*, 139.

[14] I. M. Krieger, T. J. Dougherty, *Trans. Soc. Rheology*, **1959**, *3*, 137.

[15] R. G. Larson, "*The structure and Rheology of complex fluids*" Oxford University Press, Oxford 1999, Chapter 6.

[16] L. Raynaud, B. Ernst, C. Vergé, J. Mewis, *J. Coll. Interface Sci.*, **1996**, *181*, 11.

[17] W. Richtering, K. Berend, K., *Prog. Colloid & Polym. Sci.*, **1995**, *98*, 79.

[18] D. Quemada, *Rheol. Acta*, **1977**, *16*, 82.

[19] W. Liang, T. F. Tadros, P. F. Luckham, *J. Coll. Interface Sci.*, **1992**, *153*, 131.

[20] G. Fritz, V. Schädler, N. Willenbacher, N. J. Wagner, *Langmuir*, **2002**, *18*, 6381.

[21] B. E. Rodriguez, E. W. Kaler, M. S. Wolfe, *Langmuir*, **1992**, *8*, 2382.

[22] G. L. Flickinger, C. F. Zukoski, *J. of Rheology*, **2002**, *46*, 455.

[23] S. Neuhausler, W. Richtering, *Coll. Surf. A: Physicochem Eng. Asp.*, **1995**, *97*, 39.

[24] F. M. Horn, W. Richtering, J. Bergenholtz, N. Willenbacher, N. J. Wagner, *J. Coll. Interface Sci.*, **2000**, *225*, 166.

[25] R. J. Farris, *Trans. Soc.Rheology*, **1968**, *12*, 281.

[26] R. D. Sudduth, *J. Appl. Polym. Sci.*, **1993**, *48*, 25.

[27] R. D. Sudduth, *J. Appl. Polym. Sci.*, **1993**, *48*, 37.

[28] R. D. Sudduth, *J. Appl. Polym. Sci.*, **1993**, *50*, 123.

[29] A. J. Poslinski, M.E. Ryan, R. K. Gupta, *J. Rheology*, **1988**, *32*, 751.

[30] F. M. Horn, W. Richtering, *J. of Rheology*, **2000**, *44*, 1279.