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SHORT COMMUNICATION

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Characterization of particle size and size distribution of multi-sized polymer lattices by centrifugation plus quasielastic light scattering

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Abstract A method for characterizing the particle size and size distribution of multi-sized polymer lattices was developed by combining quasielastic light scattering (QELS) with a centrifuge. Lattices were first fractionated by centrifugation and the different populations of particles were separated in successive steps. The size of these particles was measured by QELS, and the mass fraction of the particles was determined gravimetrically. The particle size and size distribution of several blends of monodisperse lattices and two industrial multi-sized lattices have been measured by this method. The results show that the particle sizes obtained using this method are in good agreement with the expected particle diameters, and that the relative amounts of the different groups of particles in the blends can be accurately determined. The efficiency of centrifuge-QELS was also confirmed by comparison with other techniques such as transmission electron microscopy (TEM), QELS, field-flow fractionation (FFF) and capillary hydrodynamic fractionation (CHDF). However, this method is not suited for the analysis of continuous, broad distributions or mixtures with a high number of different populations. It is better suited for distributions with a small number of families of particles, and then can be used for preparative propose on a laboratory scale.

Key words Characterization – particle size distribution – multi-sized – latex – centrifuge – quasielastic light scattering

Introduction

The measurement of particle size and size distribution is one of most important tasks for the characterization of lattices. Many latex properties, including rheological characteristics, mechanical strength and optical quality of films formed from them are significantly affected by the particle size and size distribution. Various methods for the determination of particle size and size distribution have been reviewed by Barth and Sun [1], Orr [2], Collins et al. [3]. Microscopy, sedimentation and light scattering are among the techniques the most commonly used to analyze the particle size. Of these, the quasielastic laser light scattering (QELS), which does not require extensive calibration, long analysis time and considerable operator skill, provides a precise and rapid means for the determination of particle size [4, 5]. However, it often fails to reveal the correct particle size distribution when a multi-sized latex is measured. Although fractionation methods such as field-flow fractionation (FFF) [6–8], analytical ultracentrifugation [8–10] and capillary hydrodynamic fractionation (CHDF) [11–13] can solve this problem and deliver results even for lattices with complicated distribution, these techniques are relatively new and can only be found in a few laboratories. Furthermore, the precision of these measurements

depends to a certain extent on calibration and operator skill.

The purpose of this paper is to present a method for the analysis of particle size and distribution of bimodal (or trimodal) polymer lattices by combining QELS with a centrifuge. This method is simple, easy and realizable in most laboratories, requiring no special equipment for particle size distribution analysis. It has some limitations such as the fact that it remains an off-line technique, and it is difficult to apply to complicated PSD. Furthermore, this method can be used on a preparative laboratory scale, provided the number of populations to be separated is limited.

Experimental

Technical-grade monomers were used in this work. Styrene (St, ACROS) contained 10–15 ppm *p-tert*-butylcatechol as inhibitor. Butyl acrylate (BA, ACROS) and methyl acrylate (MA, ACROS) contained 25–40 ppm *p-tert*-butylcatechol. Methacrylic acid (MMA, JANSSEN CHIMCA) contained 250 ppm MEHQ. Ammonium persulfate (APS, MERCK), emulsifier HV25 (polyoxyethylene alkylphenyl ether from SCHERING) and NOS25 (sodium salt of sulfated polyoxyethylene alkylphenyl ether from SCHERING) were also used as received. Deionized water was used throughout the work.

Polymerizations were carried out in a 1 l glass reactor equipped with a reflux condenser, an anchor stirrer, sampling device, nitrogen inlet and two feed inlet tubes. The recipes for the polymerization are given in Table 1. For latex SP, MP-2 and LP, a seeded semicontinuous emulsion polymerization process was used. The seed (7.5% of the total monomers, initiator and 25% of the total surfactants, water) was charged into the reactor under nitrogen atmosphere, heated to 70 °C, maintained at that temperature for 15 min for latex SP, MP-2 and 1.5 h for latex LP, and then heated to 80 °C and the feed was started. The feed was divided into two streams. The first was a preemulsion of the monomers, surfactant and water. The second was an aqueous solution of the initiator. The flow rates of these streams were adjusted to complete the addition of both streams in 5 h. The polymerization was then continued in batch for another 2 h. For latex MP-1, a batch emulsion polymerization process was used at 70 °C for 6 h.

The lattices obtained are monodisperse, and blends of these dispersions were used as the model latex for the determination of the particle size and size distribution. The small particles were separated from the large ones by centrifugation using a Beckman JA-21 centrifuge. In order to carry out these separations, the latex samples were diluted to a solids content 15–17%. The particle size was measured by using quasielastic laser light scattering (QELS) on a Brookhaven BI 8000 apparatus, and also by transmission electron microscopy (TEM, HITACHI HU12, at least 200 particles/sample were measured in order to calculate PSD), capillary hydrodynamic fractionation (CHDF, CHDF-1100) and flow field-flow fractionation (FFF, F1000 universal fractionator). The mass fraction of particles was determined gravimetrically.

Results and discussion

Table 2 shows the particle sizes of four model lattices. It can be seen that all four lattices are monodisperse and the

Table 1 Recipes for the polymerization of the monodisperse lattices

Run	St	BA	MAA	NOS25	HV25	APS	H2O	Solids content [%]
SP	67.4	32.4	0.2	4.4	5.1	0.67	110	50
MP-1	67	33	0	0.2	1.8	0.55	300	25.5
MP-2	66	33	1	2.5	2.2	0.6	110	50
LP	66	32.5	1.5	0.24	1.4	0.56	92	52.5

Table 2 Particle sizes of latex

Latex	QELS		TEM		CHDF	FFF	
	D_p [nm]	Polydispersity[a)]	D_n [nm]	D_w/D_n	D_p [nm]	D_p [nm]	Standard deviation [nm]
PP	75	0.017	–	–	75	71	12
MP-1	152	0.019	150	1.024	–	159	18
MP-2	135	0.022	–	–	133	–	–
LP	340	0.004	332	1.011	330	371	48

[a)] Given by instrument and see ref. [5] for its meaning.

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QELS gives a very close diameter for mono-sized lattices as does TEM, CHDF and flow FFF.

In order to generate the bimodal and trimodal size distributions, the monodisperse lattices were blended at different ratios. The lattices obtained were characterized by QELS, and the results are presented in Table 3. It was found that the bimodal or trimodal size distribution could not be detected by QELS unless the particle sizes of the mixed latex were significantly different from each other. All blends of latex SP/MP-1, MP-1/LP and SP/MP-1/LP seem to be monomodal, although they are composed of different-sized particles. This indicates that QELS is poorly adapted for characterizing the particle size distribution of a multi-sized latex. For the blend of latex SP/LP, a bimodal size distribution was found, but the size of the larger particles was underestimated when they are present at relatively low concentration.

It is well known that, in a latex, larger particles sediment faster than smaller ones. This means that the particles with different sizes can be separated by centrifugation. Figure 1 shows the mass fraction of particles precipitated as a function of the conditions of centrifugation. These results can be used to determine the conditions of centrifugation suitable for separating the different groups of particles.

Table 4 shows how well the blends of the model lattices were separated. The results indicate that particles with different diameters could be separated effectively by choosing appropriate centrifugation conditions. In order to calculate the concentration of each group of particles, it was supposed that the concentration of the small particles in the precipitate was half that in the upper layer after centrifugation. This is a reasonable hypothesis because the large particles would take the place of the smaller ones when

Table 3 Particle size and size distribution of the blends of the model lattices determinated by QELS

Latex	Ratio of the particles		D_p (nm)		Polydispersity
	In weight	In number	1st peak	2nd peak	
SP/MP-1	1/1	8.3/1	128		0.183
SP/MP-1	1/5	1.7/1	134		0.189
MP-1/LP	1/1	11.2/1	164		0.254
MP-1/LP	1/5	2.2/1	219		0.167
SP/MP-1/LP	1/1/1	93/8.3/1	143		0.173
SP/MP-1/LP	1/1/2	46.5/4.2/1	157		0.114
SP/MP-1/LP	1/1/4	23.3/2.1/1	78	254	1.000
SP/LP	4/1	373/1	68	258	0.987
SP/LP	1/1	93/1	67	308	0.976
SP/LP	1/4	23.3/1	68	334	1.000
SP/LP	1/19	4.9/1	51	366	1.000

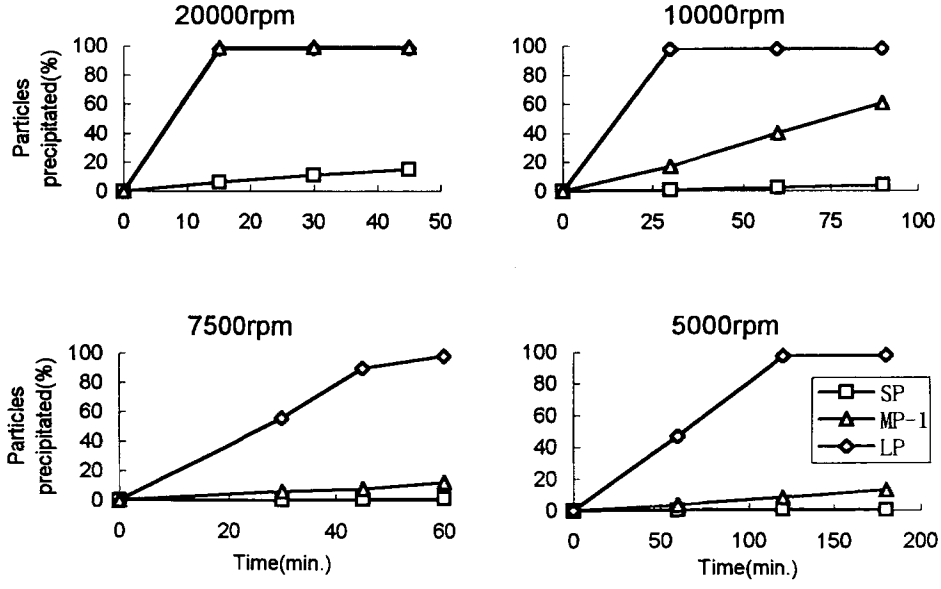

Fig. 1 Mass fraction of particles precipitated as a function of the condition of centrifugation. Solids content = 16.74% (SP), 17.33% (MP-1) and 17.33% (LP)

Table 4 Separation of the blends of lattices by centrifugation

Weight ratio of particles in blend	Condition of the centrifugation	Solids content before centrifugation (%)	Solids content after centrifugation (%)	
			Experimental	Calculated
SP/LP = 2/1	10000 rpm, 1 h	16.94	11.14	11.50
SP/LP = 1/1	10000 rpm, 1 h	17.04	8.69	8.77
SP/LP = 1/2	10000 rpm, 1 h	17.13	5.84	5.95
SP/LP = 1/3	10000 rpm, 1 h	17.18	4.50	4.50
MP-1/LP = 1/1	7500 rpm, 1 h	17.33	9.11	8.29
MP-1/LP = 1/2	7500 rpm, 1 h	17.33	6.32	6.16

they were sedimented during centrifugation. However, a certain number of small particles will still remain in the voids of the large particles. All the lattices were diluted to a solids content near 17% before centrifugation in order to (1) eliminate the influence of viscosity; and (2) diminish the error introduced by the hypothesis. The maximum calculation error caused by this hypothesis is 4.5% at a solids content 17%.

In order to examine the efficiency of separation, a ternary mixture of model lattices was subjected to field-flow fractionation analysis both before and after centrifugation. As can be seen from Fig. 2, the three groups of particles were completely separated under the indicated centrifugation conditions, and the centrifugation process did not affect the particle size and size distribution of each group of particles presented.

As mentioned earlier, the QELS technique does not give a correct particle size distribution for the bimodal or trimodal lattices. But if different populations of particles were first separated by centrifugation, and then characterized

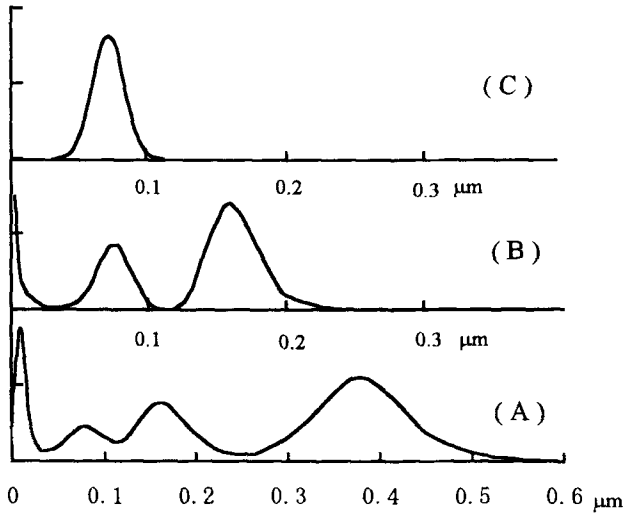

Fig. 2 FFF fractograms of a ternary mixture (SP/MP-1/LP = 2/2/6). (A) Ternary mixture before centrifugation; (B) upper layer after centrifugation (7500 rpm, 45 min); (C) upper layer after centrifugation (20,000 rpm, 1 h)

Table 5 Characterization of bimodal and trimodal lattices by centrifugation-QELS

Latex blends	Particles	Condition of centrifugation	Concentration [%]		Diameter [nm]	
			Known	Exp.	Known	Exp.
SP/LP	LP	10000 rpm, 1 h	50	52.3	340	337
1/1	SP		50	47.7	75	79
SP/LP	LP	10000 rpm, 1 h	66.7	69.1	340	346
1/2	SP		33.3	30.9	75	77
SP/LP	LP	10000 rpm, 1 h	75	76.8	340	354
1/3	SP		25	23.2	75	77
MP-1/LP	LP	7500 rpm, 1 h	50	50.6	340	335
1/1	MP-1		50	49.4	152	156
MP-1/LP	LP	7500 rpm 1 h	66.7	66.7	340	349
1/2	MP-1		33.3	33.3	152	164
SP/MP-1	LP	7500 rpm, 1 h	33.3	34.6	340	346
/LP	MP-1	20000 rpm, 0.5 h	33.3	32.7	152	149
1/1/1	SP		33.3	32.7	75	77
SP/MP-2	LP	7500 rpm, 1 h	80	81.3	340	332
/LP	MP-2	20000 rpm, 1 h	10	7.2	135	138
1/1/8	SP		10	11.5	75	79

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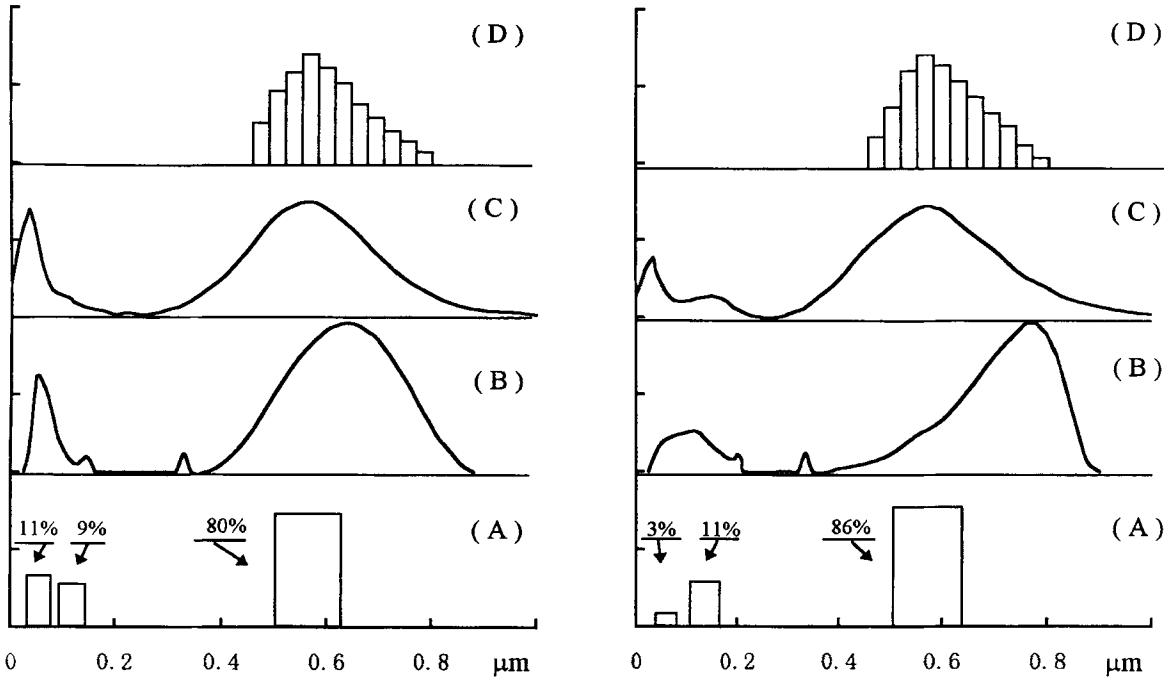

Fig. 3 Characterization of two industrial lattices by different methods. Left: latex TE-1; Right: latex TE-2. (A) QELS-centrifugation; (B) CHDF; (C) flow FFF; (D) TEM

by QELS, the size and size distribution could be obtained. Table 5 shows the results of this kind of characterization. Comparison of the results with the original values of the latex present in the blend shows a reasonable agreement. Note that the large particles must be centrifuged and redispersed several times in order to completely eliminate the small particles, the presence of which might influence the precision of the QELS measurement of the large particle diameters.

The high performance of the centrifuge-QELS method was further demonstrated by the separation and gravimetry of two multi-sized lattices obtained from ELF ATOCHEM (TE-1, solids content = 66%, and TE-2, solids content = 68%). The results of these measurements are given in Fig. 3. Also shown in Fig. 3 are the fractograms from CHDF, FFF and TEM for the same lattices. The diameter and fraction of small particles are difficult to determine by TEM because of their smaller size and irregular distribution in microphotographs. It could be seen from the results that the particle size and size distribution obtained from QELS-centrifuger agreed reasonably with those of FFF and TEM, although the agreement with CHDF is somewhat poorer.

There are two further points which must be noted. One concerns the choice of the conditions of centrifugation which can be determined experimentally. When the model of the centrifuge apparatus was changed, the conditions of centrifugation should also be adjusted for producing the same relative centrifugal field. Another concerns the T_g of polymer. When a polymer with $T_g < 0\,^{\circ}C$ was measured, the redispersion of the particles was not easy. It is therefore advisable to dilute latex using a surfactant solution; this may be efficient for helping the redispersion.

Conclusion

The centrifuge-QELS technique reported in this paper demonstrates the potential of this method as a simple and attractive tool for characterizing multi-sized polymer lattices, although the effectiveness of this technique is dependent to a certain extent on the relative size of each particle's population present in the latex and the T_g of the polymer. Compared to QELS, this method is far more precise and has a better resolving power, but it cannot be carried out on-line in a production process, as possibly CHDF and FFF can be adapted. On the other hand, if the number of populations of particles is small (2 or 3 families) the separation can be carried out easily as a preparative laboratory scale.

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