Distribution analysis of poly(vinyl chloride) latexes by transmission methods of light scattering

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The distribution analysis of particle size of some poly(vinyl chloride) latexes was performed with a modified photometer Spekol. The relationships between the turbidity ratio and the medial and latitudinal parameter of lognormal distribution of negative order or analogously between turbidity and wavelength of radiation served as working curves. The results obtained by the method of turbidity ratios were in excellent agreement with the data determined by electron microscopy or resulting from the dependence of light scattering on angle. It has been confirmed that this method gives mean mass diameter of particle size.

На усовершенствованном фотометре Спекол был проведен анализ распределения по величине частиц полихлорвиниловых латексов. Рабочими кривыми служили зависимости между мутностным отношением и медиальным и поперечным параметрами логнормального распределения отрицательного порядка, или же зависимость мутности от длины волны излучения. Результаты, полученные методом мутностных отношений, замечательно согласовывались с данными электронной микроскопии и угловой зависимости светорассеяния. Было подтверждено, что этот метод дает усредненное по массе значение величины частиц.

The distribution analysis of colloid dispersions is widely used. For instance, it is known [1] that many properties of vinyl plastisols are significantly affected by size or distribution of the size of PVC particles. The transmission methods of light scattering represent a preferred manner of determination of these parameters not only from the view-point of experiments, but also from the view-point of unambiguity of results [2]. In relation with paper [3] which is of theoretical character, this paper deals with the application of spectroturbidimetry to the distribution analysis of PVC dispersions.

Turbidity of polydisperse latex from the stand-point of the Mie theory of light scattering

In calculating the turbidity of a polydisperse system of spherical particles we started with the equation

$$\mathrm{d}\tau = (\lambda_0/2\pi n_0)^2 Q\alpha^2\pi \,\mathrm{d}N \tag{1}$$

where Q is scattering efficiency, $\alpha = 2\pi r n_0/\lambda_0$ (λ_0 — wavelength of radiation *in vacuo*, r — radius of particles, n_0 — index of refraction of medium)

$$\mathrm{d}N = k_1 \frac{\lambda_0}{2\pi n_0} \mathrm{f}(\alpha)\,\mathrm{d}\alpha \tag{2}$$

(N — number of particles in volume unit, k_1 — conversion constant)

$$\mathrm{f}(\alpha) = (K/\pi)^{1/2}\alpha^{-1} \exp\left[-K \ln^2 \alpha/\alpha_{\mathrm{M}}\right] \tag{3}$$

(α_{M}, K — parameters of lognormal distribution of negative order)
On rearrangement we may write

$$\frac{\tau}{\varrho} = \left(\frac{\lambda_0}{2\pi n_0}\right)^3 \frac{\pi k_1}{\varrho}\int_0^\infty Q\alpha^2 \mathrm{f}(\alpha)\,\mathrm{d}\alpha \tag{4}$$

The concentration ϱ was expressed on the basis of validity of the relation $\varrho/\varrho_0 = VN$ for monodisperse system (ϱ_0 is density and V is the volume of particles). Simultaneously it holds for polydisperse system [3]

$$\frac{\varrho}{\varrho_0} = \int_\infty^1 V\,\mathrm{d}N = \frac{4\pi\lambda_0^4 k_1}{3(2\pi n_0)^4}\int_0^\infty \alpha^3 \mathrm{f}(\alpha)\,\mathrm{d}\alpha \tag{5}$$

By inserting for ϱ (at infinite dilution) into eqn (*4*), we obtain

$$\left(\frac{\tau}{\varrho}\right)_0 = \frac{3\pi n_0}{2\lambda_0\varrho_0}\,\frac{\displaystyle\int_0^\infty Q\alpha^2\mathrm{f}(\alpha)\,\mathrm{d}\alpha}{\displaystyle\int_0^\infty \alpha^3\mathrm{f}(\alpha)\,\mathrm{d}\alpha} = \frac{3\pi n_0}{2\lambda_0\varrho_0}\left(\frac{\bar{Q}}{\bar{\alpha}}\right) \tag{6}$$

while it holds for $(\bar{Q}/\bar{\alpha})$ [3]

$$\left(\frac{\bar{Q}}{\bar{\alpha}}\right) = \frac{\displaystyle\int_0^\infty Q\alpha^2\mathrm{f}(\alpha)\,\mathrm{d}\alpha}{\sqrt{\dfrac{\pi}{K}}\,\alpha_{\mathrm{M}}^3 \exp\left(\dfrac{9}{4K}\right)} \tag{7}$$

By using eqn (*6*), we can construct working curves for the method of turbidity ratios as well as the method of specific turbidity [4]

$$(\bar{Q}/\bar{\alpha})_{\lambda(01)}/(\bar{Q}/\bar{\alpha})_{\lambda(02)} = \mathrm{f}(r)$$

or $\qquad$ (*8*)

$$(\bar{Q}/\bar{\alpha}) = \mathrm{f}(\lambda_0)$$

Experimental

The transmission was measured at eight wavelengths (436—680 nm) and laboratory temperature with a modified spectrophotometer Spekol (Zeiss, Jena). In order to remove the interfering influence of small angle light scattering, we placed a tube of 25 cm length in front of the photocell and replaced the original spherical slit behind the measuring cell (in direction to detector) by a rectangular slit (15 mm × 1.5 mm). The calculations according to paper [5] showed that almost no scattered light fell on the detector provided the turbidity was measured in this manner.

The PVC latexes were identical with the latexes studied earlier [6]. The basic aqueous dispersion was once more purified by means of a membrane filter Synpor with the size of pores of 1500 nm. By diluting the basic dispersion with powderless water, we prepared the samples with concentrations in the range 10^{-5}—10^{-4} g cm^{-3}. The concentration was determined by evaporating the solvent and drying in vacuum drier at 50 °C to constant mass.

Results

The distribution analysis of the investigated latexes was carried out by comparing the theoretical and experimental values of light scattering in the sense of eqn (*6*). The integral in the numerator of this equation was solved numerically with a computer M4030-1 by the trapezoid method, a step being $\Delta\alpha = 0.1$. The coefficients of scattering were calculated from the following equation

$$Q = \frac{2}{\alpha^2} \sum_{n=1}^{\infty} (2n+1)^{-1} \cdot (|a_n|^2 + |b_n|^2) \qquad (9)$$

where a_n and b_n are the Mie coefficients.

Fig. 1 represents the theoretical relationships $(\bar{Q}/\bar{\alpha}) = \mathrm{f}(\lambda_0)$ for PVC latexes with different degrees of polydispersity, the medial radius NOLD of which was $r_M = 140$ nm. The experimental values of $(\bar{Q}/\bar{\alpha})$ calculated on the basis of measurements of specific turbidity (Fig. 2) and eqn (*6*) are denoted with circles. The optimum consistence of the experimental and theoretical values of $(\bar{Q}/\bar{\alpha})$ enabled us to determine the distribution parameters of latex *1* ($K = 50$, $D_M =$ 280 nm) and latex *2* as well (Table 1). The theoretical relationships of the method of turbidity ratios are shown in Fig. 3. It results from this figure that there are

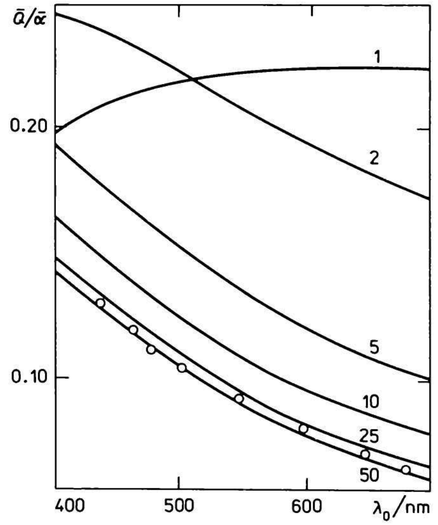

Fig. 1. Theoretical dependence of $\bar{Q}/\bar{\alpha}$ on the light wavelength for PVC latex.
NOL distribution with medial radius r_M = 140 nm and K = 1, 2, 5, 10, 25, 50; ○ experimental points.

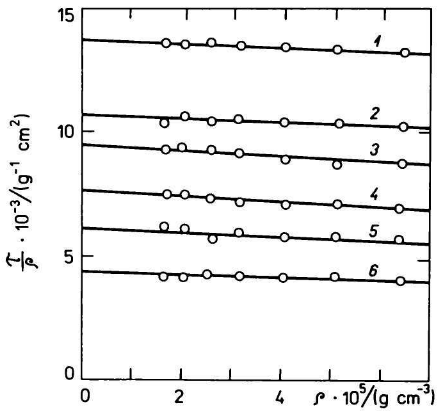

Fig. 2. Relationship between concentration and turbidity of PVC latex *1* for the light wavelengths.
1. 436 nm; *2.* 475 nm; *3.* 500 nm; *4.* 546 nm; *5.* 600 nm; *6.* 680 nm.

Table 1

Distribution parameters of PVC latexes obtained by different methods

	Method	Turbidity ratios	Spectroturbidimetry	Electron microscopy [6]	Light scattering angle dependence [6]
Latex *1*	D_M/nm	270	280	272	268
	K	75	50	—	60
Latex *2*	D_M/nm	410	420	407	395
	K	50	50	—	35

several pairs of distribution parameters for the experimentally determined turbidity ratio $(\bar{Q}/\bar{\alpha})_{436}/(\bar{Q}/\bar{\alpha})_{546} = 1.433$ (latex *1*). The plurivalidity of data was removed by comparing the theoretical and experimental data for the turbidity ratios at the wavelengths 546 nm/680 nm and 436 nm/680 nm. The plots $r_M = f(K)$ were constructed on the basis of data corresponding to individual turbidity ratios and the required parameters were found on the basis of optimum conformity of three curves. The results of this procedure for both investigated latexes are given in Table 1 together with the values of D_M and K obtained from the angle dependence of light scattering or electron microscopy. A comparison of the results indicates

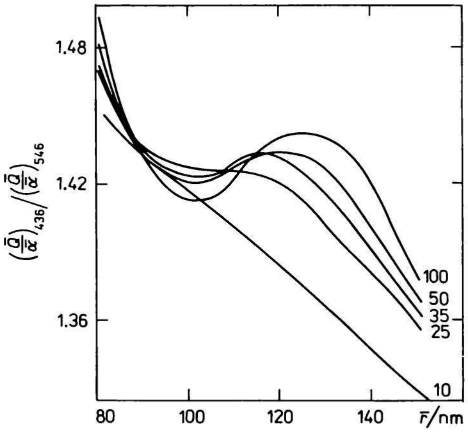

Fig. 3. Theoretical dependence of the ratio $(\bar{Q}/\bar{\alpha})_{436}/(\bar{Q}/\bar{\alpha})_{546}$ on mean radius $\bar{r}$. NOL distribution, $K = 10, 25, 35, 50, 100$.

a very good applicability of spectroturbidimetry in a detailed distribution analysis of PVC latexes.

Lecloux, Heyns, and *Gobillon* [7] also determined the mean diameter of PVC latexes from turbidity ratios. In connection with the problem which diameter is obtained by this method, they prepared four mixtures of monodisperse latexes.

On the basis of the relationship

$$\bar{D} = \sqrt[3]{\frac{\sum_{1}^{\infty} n_i D_i^x}{\sum_{1}^{\infty} n_i D_i^{x-3}}} \tag{10}$$

where n is the total number of particles, valid for $x = 6$, and validity of the relation

$$\bar{M}_w = \frac{\sum_{1}^{\infty} n_i M_i^2}{\sum_{1}^{\infty} n_i M_i} \tag{11}$$

they stated that it was the mean mass diameter because mass was proportional to the third power of the diameter of particle. Our measurements confirm this fact because the data obtained by electron microscopy and the method of light scattering (dependence on angle) are in relation with the mean mass diameter of the size of particles.

It results from Table 1 that the spectroturbidimetry gave higher values for particle diameters. It is evidently due to the influence of the drawbacks which are involved in this method when compared with the method of turbidity ratios. In this respect, we must, in the first place, mention the use of the precise value of mere polymer concentration and not of other components of latex particle [8].

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