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Direct Observation of Swelling of Non-Cross-Linked Latex Particles by Scanning Angle Reflectometry

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Introduction. The swelling of latex particles by plasticizers has been the subject of many studies over the past few decades. The most comprehensive thermodynamic analysis of this problem was made by Bindschaedler[1] in 1985. The often observed non-Fickian behavior of the swelling led to the concept of a diffusion/relaxation mechanism, of which Berens and Hopfenberg gave a phenomenological description.[2] The technique they used consisted of measuring the weight of the sample as a function of time, from which they calculated the uptake of solvent as a function of time. They saw an initial large uptake of plasticizer (diffusion controlled) by the particle, followed by a much slower uptake (controlled by network relaxations). Their conclusion was that the initial stage is totally dependent on the *free* volume in the particle, only resulting in a weight gain of the particle, without an increase in particle diameter.

We investigated the swelling of non-cross-linked polystyrene particles (size ≈ 410 nm) by methyl ethyl ketone (MEK), dissolved in water, using scanning angle reflectometry. With this technique, we measured the diameter of the particles as a function of time, from which we deduce the uptake of MEK. A great advantage of scanning angle reflectometry is that it is very sensitive to small increases in particle size (<0.1% of the diameter of the particle). Another advantage is the stability of the setup, allowing us to measure for more than a week without losing accuracy.

In contrast to the conclusion of Berens and Hopfenberg,[2] we observed an increase in the diameter of the particle in the initial stage of swelling. Although observation of very rapid growth in the beginning of a swelling experiment has also been observed by other researchers,[5−8] the consequences for the interpretation of the Berens and Hopfenberg model were never discussed. Based on our observations, we will propose a modification to the model of Berens and Hopfenberg.

Theory. In this section, we briefly summarize the main results of the thermodynamic equilibrium analysis of Bindschaedler and of the diffusion/relaxation model of Berens and Hopfenberg. For a detailed description of the analysis of the reflectometry data, we refer to recently published material.[3]

The thermodynamics of polymer particle swelling by a mixture of an organic solvent and water is discussed by Bindschaedler *et al.*[1] In the case of swelling of polystyrene, water does not enter the polymer phase, and the requirement of thermodynamic equilibrium yields

$$\ln v_{1,\mathrm{p}} - v_{1,\mathrm{p}} - \frac{1}{x_3}v_{3,\mathrm{p}} + \chi_{13}v_{3,\mathrm{p}}{}^2 + \ln v_{1,\mathrm{a}} - v_{1,\mathrm{a}} -$$

$$\frac{1}{x_2}v_{2,\mathrm{a}} + \chi_{12}(v_{1,\mathrm{a}};v_{2,\mathrm{a}})v_{2,\mathrm{a}}{}^2 = 0 \quad (1)$$

where the indices 1, 2, and 3 refer to the solvent, water, and polymer, $v_{i,\mathrm{p}}$ is the volume fraction of species i in the polymer phase, $v_{i,\mathrm{a}}$ is the volume fraction of species i in the aqueous phase, and x_i is the ratio of the molar volume of species i and the molar volume of the solvent; χ_{13} and

$$\chi_{12}(v_{1,\mathrm{a}};v_{2,\mathrm{a}}) = \left(g_{12} - v_{1,\mathrm{a}}\frac{\mathrm{d}g_{12}}{\mathrm{d}v_{2,\mathrm{a}}}\right)$$

are the Flory interaction parameters. Note that $\chi_{12}(v_{1,\mathrm{a}};v_{2,\mathrm{a}})$ is volume fraction dependent, and may be calculated from experimental data.[4] The interfacial tension term that should enter eq 1 is negligible and therefore omitted. Because water does not enter the polymer phase, $v_{1,\mathrm{p}} + v_{3,\mathrm{p}} = 1$. The same kind of reasoning holds for the aqueous phase; here $v_{1,\mathrm{a}} + v_{2,\mathrm{a}} = 1$.

Equation 1 makes it possible to predict the volume fraction of the solvent in the polymer provided one knows the various interaction parameters involved.[4]

The phenomenological diffusion/relaxation model developed by Berens and Hopfenberg[2] describes the sorption process in a glassy polymer as a combination of Fickian diffusion and relaxation processes. The relaxation process is assumed to be first order in the concentration gradient that drives the process. For the total amount of absorbed solvent, we can write, according to Berens and Hopfenberg,[2]

$$M_{\mathrm{t}} = M_{\infty,\mathrm{F}}\left\{1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\mathrm{e}^{-n^2 k_{\mathrm{F}}t}\right\} + \sum_i M_{\infty,i}\{1 - \mathrm{e}^{-k_i t}\} \quad (2)$$

where $k_{\mathrm{F}} = 4\pi^2 D/d^2$, with D and d the diffusion constant and diameter of the particle, respectively, and $M_{\infty,\mathrm{F}}$ the equilibrium amount of absorbed solvent due to Fick diffusion; k_i is the relaxation constant corresponding to the ith relaxation mode. $M_{\infty,i}$ is the equilibrium amount of absorbed solvent for the ith relaxation mode. Note that the occupied volume calculated from eq 2 should in the limit for long times converge to the volume predicted by eq 1.

Experimental Section. A complete description of our experimental setup can be found elsewhere.[3] Here we will limit ourselves to a brief discussion of the experimental procedures.

Adsorption of the latex particles was performed onto the optically flat hypotenuse of a rectangular prism made of quartz. Two such prisms were mounted in a holder, leaving a 3 mm spacing between the two hypotenuses. The prisms were cleaned with a laboratory-use detergent (Hellmanex II; Hellma GmbH, D-7840 Mullheim) and rinsed thoroughly with deionized Millipore water, a dilute sulfuric acid solution, and again water.

We measure the reflectivity of waves polarized parallel to the plane of incidence (p waves) at a number of angles around the Brewster angle of the quartz/water interface. The light source is a 5 mW He−Ne laser operating at a wavelength $\lambda = 632.8$ nm. The angles of incidence and of reflection are selected by simultaneously rotating the laser and the detector supports.

At the beginning of each experiment, reflectivities are measured for the pure quartz/water interface, allowing the determination of two instrument-depend-
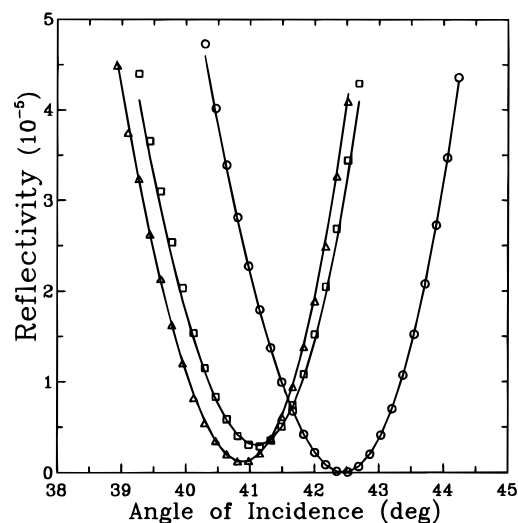
Figure 1. Reflectivity as a function of angle: (○) reflectivity of the bare surface; (△) reflectivity just before the swelling experiment; (□) reflectivity obtained with 5 vol % MEK in water.

ent constants: the residual intensity at the Brewster angle and the amplification of the signal. After this, a diluted latex suspension (1:1000 from the original 4% solution provided by the manufacturer (IDC, Portland, OR)) was injected into the cell. Particles with positively charged amidine groups were chosen in order to ensure adsorption on the negatively charged quartz.

After a coverage of about 6% was reached, the cell was again flushed with water, to remove all nonadsorbed particles. The cell was then injected with the MEK–water solution. Reflectivity curves were measured continuously, following the swelling process for about 1 week. Note that, because the amount of MEK that enters the particles is small compared to the amount of MEK present in the aqueous phase, the concentration of MEK in the aqueous phase is constant.

Results and Discussion. Examples of curves obtained using reflectometry are shown in Figure 1. During the experiment, the shape of the curves changes, and the minimum of the curves shifts and increases. These changes in the curves are directly related to the diameter of the particles and the surface coverage. The data were analyzed using the following expression for the reflectivity:[3]

$$R = r_{12}{}^2 + 2t_{12}t_{21}r_{12}\{\mathcal{R}(r_l)\cos\Delta - \mathcal{F}(r_l)\sin\Delta\} + t_{12}{}^2 t_{21}{}^2 |r_l|^2 \quad (3)$$

where $t_{12} = t_{21}$ are the angle-dependent transmission coefficients, r_{12} is the Fresnel reflection coefficient of the quartz/water interface, and $\Delta = k_2 d \cos\theta_2$ is the phase difference between the field reflected at the interface and the light coherently scattered from the spheres; θ_2 is the angle of transmission at the interface, k_2 the wavevector, and d the diameter of the particle. Information about the diameter of the particle and surface coverage can be extracted from eq 3 using

$$r_l(\theta_2) = \frac{8\varphi S_p(\pi - 2\theta_2)}{k_2{}^2 d^l \cos\theta_2} \quad (4)$$

In this equation φ equals the surface coverage, and $S_p(\theta)$ is the Mie scattering function for p-polarized light.

The electromagnetic particles–particle interactions are neglected in eq 3; the effect of these interactions is currently under investigation. For small relative changes in diameter (up to 10%), these interactions do not influence the final analysis.

The swelling as a function of time, shown in Figure 2, shows some important features: (i) There is an initial fast uptake of solvent, as observed by others.[2,5–8] This uptake results *directly* in an increase in particle size, appearing as a jump. (ii) From the logarithmic plot we see that, following the jump, two characteristic times seem to be involved.

In fitting eq 2 to the data, we needed three characteristic times. The characteristic time associated with the Fick diffusion was so small that we could obtain an equally good fit by taking the Fick contribution constant. This implies that the Fick diffusion part has already relaxed before the first data point.

The observation of *growth* of the particle during the fast initial uptake of MEK is an important feature. The first stage *following* the jump is often associated with Fick diffusion. If one plots the increase in particle size versus the logarithm of time, as is done in Figure 2, one sees that this stage already results from the relaxation mechanism.
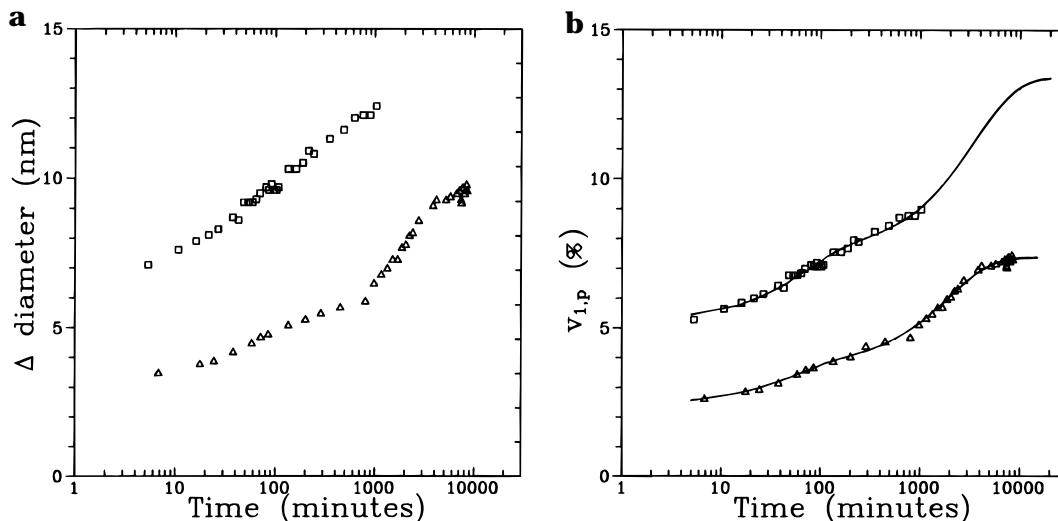

Figure 2. (a) Change in diameter of the particle and (b) the corresponding volume fraction MEK ($v_{1,p}$) in the polymer phase as a function of time for a 5% (△) and a 9% (□) MEK/water solution.

From Figure 2, we also see that the jump of the particle diameter in the beginning of the experiment is a function of the concentration of MEK in the water phase. In all our measurements, we have observed this jump, but so far we have not been able to obtain reproducible values for its *magnitude*. The magnitude of jump appears to be linear in the concentration of MEK, but because of the poor reproducibility, this conclusion is tentative.

For the 5% MEK/water solution, we observed that the swelling at long times approached the value expected from the thermodynamic equilibrium analysis (in this particular case, 7.3 vol % MEK per unit volume of polymer).

The measurement with the 9% MEK/water solution was stopped after about 1000 min. The extension of the curve was obtained by fitting with the end value calculated from the thermodynamic analysis (in this case, 13.4 vol % MEK per unit volume of polymer).

Based on our observations, we would like to propose the following modification to the "free-volume + network relaxation" model proposed by Berens and Hopfenberg. Our measurements suggest that the swelling process consists of two phases: a very fast initial growth, apparently linear in the driving force for the process, followed by a much slower growth apparently governed by relaxation processes of the polymer network. Note that this type of response to a driving force for deformation of the particle is very similar to the viscoelastic response of a polymer network to an imposed constant shear field. In such a shear experiment, the deforma-tion of the polymer as a function of time is characterized by an initial elastic stage, which is linear in the driving force, followed by a plastic stage governed by network relaxations.

Further measurements are needed to establish if the first stage of the swelling experiment is truly elastic. In particular, in a deswelling experiment performed just after completing the first stage of the swelling experiment, the particles should regain their original size.

References and Notes

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