Spectra-ellipsometry for latex film formation

The principles of spectro-ellipsometry (SE have been presented elsewhere[1]. For simplicity, in
Figure 1 a schematic representation of this measurement method is shown.

Abstract
The philosophy of the ellipsometry method consists on measuring the so-called spectroscopic parameters: Ψ and Δ using the reflection measurement with the experimental arrangement shown in Figure 1. Then, defining a good model the measured spectra of these parameters are simulated based on the optical constants and thickness of the layers that form the sample.

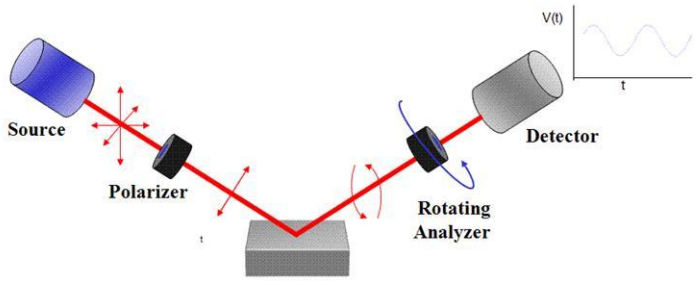

Figure 1. A schematic picture of spectroellipsometry measurement arrangement.

What about Ψ and Δ?
In ellipsometry we compare the s- and p-polarized components of the light wave. Let's define the phase difference between p- and s- wave before reflection (labeled by *0*) as δ_1 and after reflection (labeled by *r*) as δ_2, by:

$$\delta_1 = \delta_{p0} - \delta_{s0} \tag{1}$$

$$\delta_2 = \delta_{pr} - \delta_{sr} \tag{2}$$

From here, it is easy to define the parameter Δ which describes the phase introduced by reflection:

$$\Delta = \delta_1 - \delta_2 \tag{3}$$

A complete comparison between p- and s- polarized waves of the reflected beam is obtained when the modulus (amplitude) is considered. Therefore, the Ψ parameter defined as:

$$\tan\Psi = \frac{|R^p|}{|R^s|} \tag{4}$$

will help to introduce the *fundamental equation of the ellipsometry:*

[1] N. Tomozeiu, private publications, or
Ellipsometry - Wikipedia

$$\rho = \frac{R^p}{R^s} = \tan\Psi \cdot exp(j\Delta) \quad (5)$$

By simulating the spectra of Ψ and Δ considering the optical model of the sample, the output is the refractive index of the sample. Moreover, having a sample that changes the composition in time, the refractive index changes, too.

Considering as sample polymer particles dispersed in water, the evolution in time of the refractive index can be modeled. When the water is totally evaporated the film can be seen as being formed from two distinct parts[2] as shown in Figure 2.

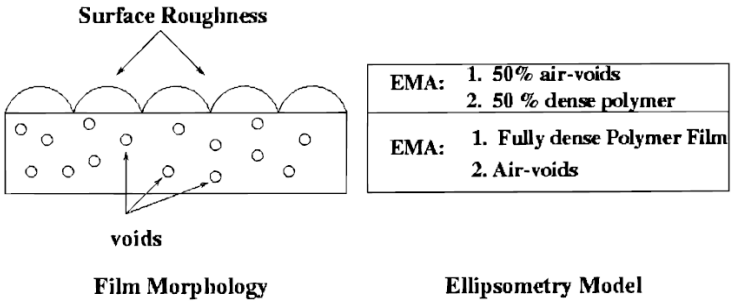

Figure 2. The film morphology according to the AFM pictures and its model for ellipsometry measurements.

Following the publication of Tzitzinou et al[2], in the right side of Figure 2 it is shown the model used to describe the surface and the bulk of the latex layer: i) the surface is described as an EMA model with 50% voids and 50% dense polymer material. We fit for the effective thickness of the top layer, which corresponds to surface roughness; ii) the bulk is described with an EMA model for a continuous, dense polymer phase (n =1.5) containing voids with n =1. We fit for the volume concentration of voids.

An example of the calculated refractive index is shown in Figure 3 for three different situations, as described in Tzitzinou et. al. The authors used mixtures of water with LgSf particles as polymeric colloids (shown by ◇). Data obtained from the same particles' film formed at 60 °C are shown for comparison with (○). Also, mixtures of a bimodal blend of 99 wt % LgSf and 1 wt % SmSf particles have been investigated and the data are plotted with (▲). All experiments were performed with light of 500 nm wavelength.

The refractive index of the polymeric particles is 1.489, that of water is 1.33 and of air is 1. At the beginning of the experiment there is a lot of water, so the refractive index is close to 1.33. When water evaporates the mixture is poorer and poorer in water and this is equivalent with increasing of the refractive index. At 60^0C all the water is evaporated, the film is formed and the refractive index amounts 1.489.

After about 20 min, drying nears completion. The freshly formed films have significant interparticle voids. The decrease in <n> is consistent with the replacement of water initially present in the interparticle space – by air voids; an increase of air voids causes a reduction in refractive index. The minimum in <n> is attributed to the completion of water evaporation. After this, the particles are expected to eliminate the voids, showing that the particles are deformable. Coalescence of particles is indicated by a very gradual increase of the refractive

2 A. Tzitzinou et al. Macromolecules 2000, 33, 2695-2708

index (as time, this could take hours depending on the layer composition). When all the voids are eliminated and the film is fully dense the refractive index eventually reaches its maximum value (1.489 at 500 nm).

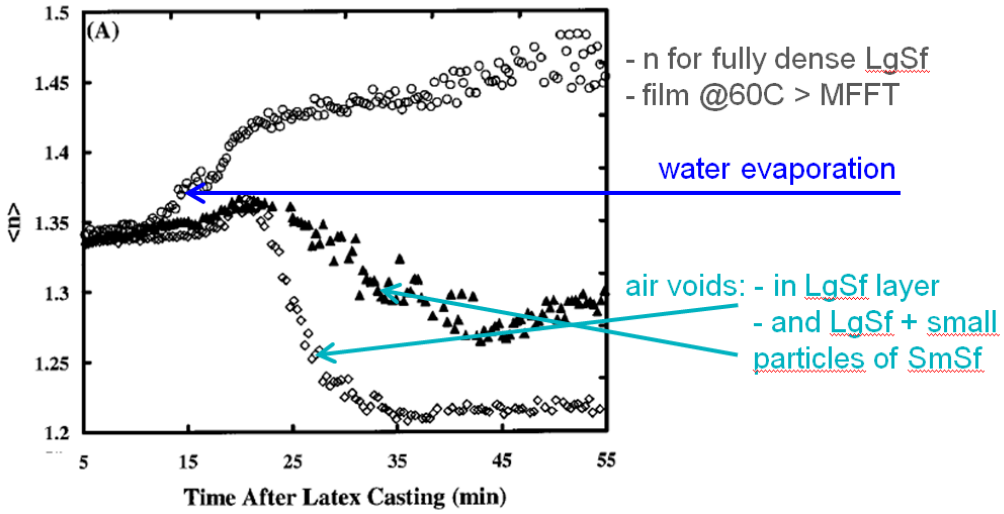

Figure 3. The refractive index as a function of time for three different films: (◇) LgSf particles as polymeric colloids in water; (O) the same particles but film formed at 60°C; (▲) a bimodal blend of 99 wt % LgSf and 1 wt % SmSf particles .

By adding of just 1 wt % small particles, Figure 3 shows that <*n*> decreases less upon film formation. This finding is consistent with fewer interparticle voids caused by small particles packing around the large ones.
At the elevated temperature, void coalescence is expected to proceed at an enhanced rate. Figure 3 shows that, in this case, <*n*> increases throughout film formation. This steady increase provides evidence that there is not significant void formation accompanying water loss. After 55 min, the refractive index is close to the value of the fully dense polymer (1.489 at 500 nm), indicating that particle coalescence is nearly complete.

In literature there are few papers that deal with the SE technique measuring and analysing the latex film formation. In our view, this method is dedicated to fundamental research and, as usual, the approximation used in determining the refractive index from the ellipsometry parameters has to be experimentally validated.