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# Spectroscopic Ellipsometry for Characterization of Thin Films of Polymer Blends

*K. Hinrichs,*[1] M. Gensch,[1] N. Nikonenko,[2] J. Pionteck,[3] K.-J. Eichhorn[3]*

**Summary:** Morphology, composition, miscibility, interdiffusion, and interactions at interfaces are important quantities of polymer blends. Many of these parameters can be probed with spectroscopic ellipsometry. Ellipsometry in the visible spectral range is very suitable for determination of thicknesses and the high frequency refractive indices of thin organic films. However the spectral contrast is low for many polymers in comparison to infrared spectroscopic ellipsometry (IRSE) where specific contributions of the molecular vibrations are probed. In the presented study the infrared optical constants of a double layer (206.6 nm in total) of poly(*n*-butyl methacrylate) (PnBMA) and poly(vinyl chloride) (PVC) and of the films of the single compounds have been determined with optical simulations using layer models. The multiple layer model served for simulation of the ellipsometric spectra taken after an annealing induced mixing process in a polymeric double layer. The ellipsometric spectra of a not completely mixed sample could be fitted in a three-layer model, in which a mixed interphase in between the two layers of the polymers is formed due to interdiffusion.

**Keywords:** blends; films; infrared spectroscopy; mixing; simulations

## Introduction

The molecular and geometric structure of ultra-thin films and organic multilayers is a very important property in nanotechnology and polymer science. In principal these properties can be investigated by infrared spectroscopic ellipsometry (IRSE). This is emphasized by recent articles showing some possibilities of the ellipsometric technique for studies of mixing in miscible polymers[1,2] and the composition of stimuli responsive changes in mixed polymer brushes.[3]

A standard application of ellipsometry is the determination of the optical constants of a material from measurements of bulk samples and thin films. Optical constants of isotropic organic films on various substrates in the mid infrared region have been determined for several materials, for example for nylon,[4] poly(dimethyl siloxane),[5] polytetrafluoroethylene,[6] poly (vinyl acetate),[7] surface-fluorinated polyethylene,[8] gelatine,[9] and silicone.[9] Furthermore, in some cases also the anisotropic optical constants were determined (for example of a polyimide in Ref. 10). The investigation of layered samples is even more sophisticated, because the geometry of the sample has to be implemented into the optical model used for the simulation. One additional difficulty is that typically the result of such complex optical simulations is not unequivocal. However, this article shows that a check of a possible optical model can be made by simulation of ellipsometric spectra. This is shown exemplarily for the spectral range from 1300–1100 cm$^{-1}$, in which characteristic structurally sensitive molecular vibrations of the ester group occur, which are important to monitor the molecular interactions in a blend of poly(*n*-butyl methacrylate) (PnBMA) and poly(vinyl chloride)

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[1] ISAS – Institute for Analytical Sciences, Department Berlin, Albert-Einstein-Str. 9, 12489 Berlin, Germany
Fax: (+49) 3063923544
E-mail: hinrichs@ansci.de

[2] B. I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, 68 Nezalezhnasti Avenue, 220072 Minsk, Belarus

[3] Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, 01069 Dresden, Germany

(PVC). In a previous paper[2] it has been found that during the annealing process in the double layer of poly(*n*-butyl methacrylate)/poly(vinyl chloride) (PnBMA/PVC) interdiffusion occurs and in between two polymers an interlayer is formed. In the given work the simulations will be performed for thin films of pure polymers, PnBMA/PVC double layer, and PnBMA/mix/PVC multiphase system with the aim of the determination of a possible optical model.

## Experimental

### Materials and Film Preparations

PVC (Aldrich, $\eta = 0.51$, catalog 38.929-3) and PnBMA (Polyscience, $= 0.50$, catalog # 02061) were precipitated from THF solution into methanol before use. The molecular weights $M_w/M_n$ were 63000/32000 (g/mol) and $M_w/M_n = 205000/103000$ (g/mol), and the glass transition temperatures $T_g$ were 84 °C and 38 °C, respectively.

For the ellipsometric studies thin polymer films of PVC and PnBMA were prepared by spin coating (1800 rpm, 60 s, room temperature) on gold-coated glass slides (PVC from THF/tetrachloroethane solution, PnBMA from di(n-butyl ether) solution). The layers were slowly dried in vacuum with a temperature of 60 °C for 1 h. A double layer system (PnBMA/PVC) was prepared by subsequent coating: first the PVC layer, then the PnBMA layer. The thickness of the layers was examined by ellipsometry and the homogeneity by atomic force microscopy. In order to study the interdiffusion between both polymers the double layer under study has been annealed at 110 °C, which is above the glass transition temperatures of both polymers. The annealing time was increased sequentially from 1 min up to 30 min.

### IR-Ellipsometry

Upon reflection at a plane surface, linearly polarized radiation generally becomes elliptically polarized. Its polarization state can be described by two ellipsometric parameters: amplitude ratio ($\tan\Psi$) and phase shift difference ($\Delta$) of two mutually orthogonal polarized components of the reflected waves ($r_s$ and $r_p$). In our photometric ellipsometric measurements, the sample is irradiated by linearly polarized radiation and the reflected beam is analysed by a second polarizer placed behind the sample. The ellipsometer is attached externally to a Bruker IFS 55 Fourier Transform interferometer. Details about the measurement and set-up are described elsewhere.[11,12]

The ellipsometric spectra were recorded by a DTGS detector at a spectral resolution of 2 $\text{cm}^{-1}$. The measurements were performed at an angle of incidence of 70°.

### VIS Ellipsometry

Variable Angle Spectroscopic Ellipsometry (VASE) in the visible spectral range was done using a rotating analyzer type 44-wavelength ellipsometer M-44 (Woollam Co.). Our instrument is equipped with an automated computer-controlled goniometer, a horizontally mounted sample stage and 75 Watt Xenon short arc lamp. Radiation below 400 nm was removed by a WG 360 Schott glass filter before it reached the polarizer. After reflection from the sample and passing through the analyzer the light was dispersed onto a detector array which permits fast measurements simultaneously at 44 wavelengths between 428 and 763 nm. The $\Delta$ and $\tan\Psi$ spectra were measured at three angles of incidence (65°, 70°, and 75°) at 22 °C and 40–50% r.h.

First of all, the optical constants of the uncoated gold substrates were determined. In a second step the thickness d and refractive index n of single non-absorbing ($k = 0$) films of PVC and PnBMA on gold were determined from fits of the measured spectra using a two-parameter Cauchy function, which is often applied to consider the wavelength dependence of n: $n(\lambda) = A + B/\lambda^2$. Based on the obtained refractive indices for PVC ($n = 1.546 + 0.004/\lambda^2$) and for PnBMA ($n = 1.483 + 0.003/\lambda^2$) the thickness of both sublayers in the double layer PVC/PnBMA prepared on gold could be determined. The frequency independent part was taken as the high frequency refractive index in the simulation of the infrared ellipsometry results ($n_\infty = 1.483$ (PnBMA) and $n_\infty = 1.546$ (PVC)).

### Simulation

For interpretation the measured ellipsometric spectra were simulated. Note, that only in the case of isotropic bulk samples for which the influence of the surface on the optical spectra is negligible, the optical constants can be determined directly from the measured ellipsometric spectra.[13] The simulations presented in this work are based on special solutions of the 4×4 matrix formalism, the inclusion of vibrational bands by harmonic oscillators, and the use of an optical multilayer model (Figure 1). Further details about the simulations can be found elsewhere.[10]

## Results

### Optical Constants of the Single Polymers: PVC and PnBMA

To simulate the ellipsometric spectra of a polymeric double layer the optical constants of the single compounds should be known. In order to obtain them, measurements of films of the single compounds (104.1 nm PVC and 98.48 nm PnBMA) on gold were performed. From these measurements the optical constants of PVC and PnBMA were determined by best-fit simulations[10] (Figure 2). The high frequency refractive indices (indicated by dashed lines in the figure) were taken from the results of VIS ellipsometry of the same films.

The PnBMA absorption bands in the 1300–1100 $\text{cm}^{-1}$ range are associated with CO and CC stretching modes in the ester groups and are expected to be very sensitive to conformational changes.[14,15] For PVC film the most intense band near 1256 $\text{cm}^{-1}$ is due to the CH deformation vibrations.[16]

### The Double Layer: PnBMA/PVC on Gold

Figure 3 shows the measured and simulated ellipsometric spectra for the double layer of PnBMA and PVC on Au. The optical constants of the substrate were determined from the gold substrate prior to deposition of the polymers and the optical constants of the single compounds were used as input

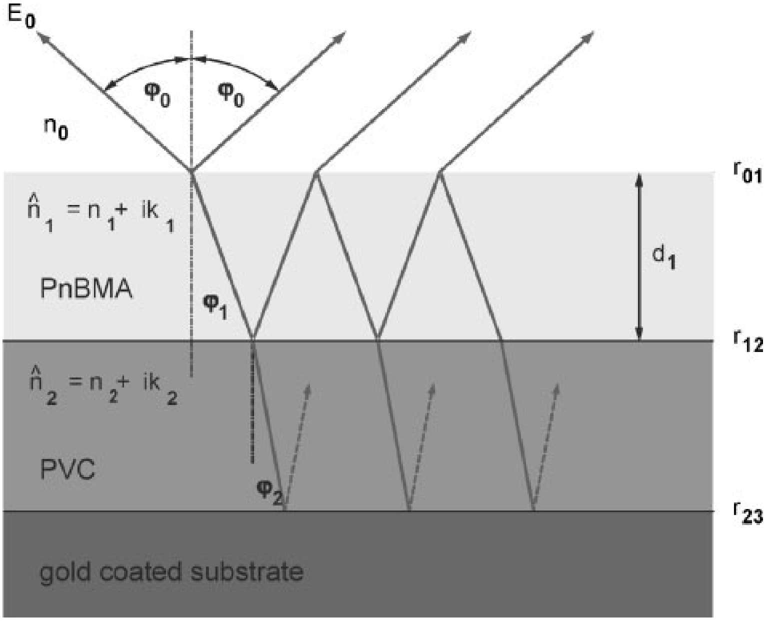

*Figure 1.*
Schematic of the double layer model as used in the calculations of the initial double layer of PnBMA/PVC on gold.

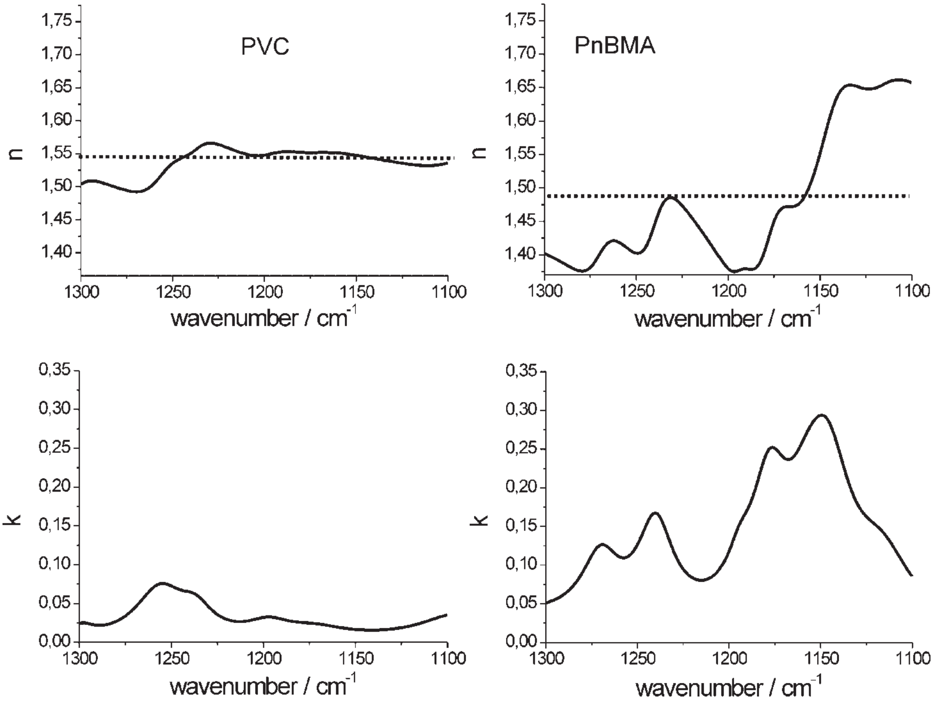

***Figure 2.***
Optical constants of PVC and PnBMA. The data were calculated from measured spectra of films of the single compounds on gold. Dashed lines mark the high frequency refractive indices.

data for the simulations. Note that the double layer was prepared in a stepwise procedure and that incompatible solvents for the two compounds have been used in order to prevent mixing between the two compounds. Because of this careful preparation the initial sample is believed to be described correctly by a double layer (Figure 3b) of the two polymers without or with only a very thin intermixed region between the two single layers.

In general a good agreement between the measured and simulated spectral signatures is seen in Figure 3, which proves that the film can be described within a double layer model. Small deviations

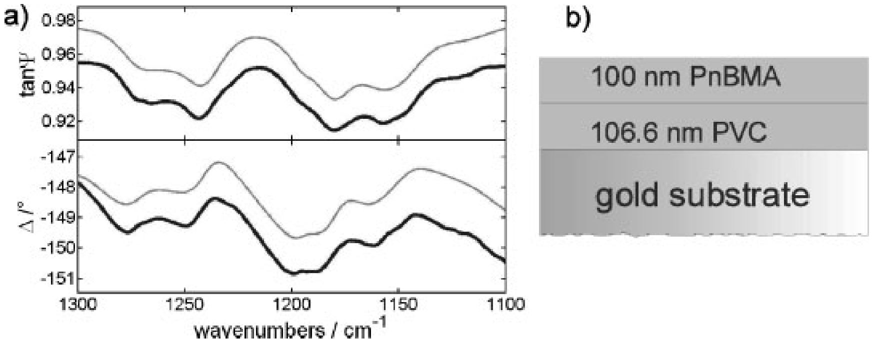

***Figure 3.***
a) Measured (thick black lines) and simulated spectra (thin grey lines) for the polymeric double layer of PnBMA on PVC on gold. b) model for simulation.

between simulation and measurement are observed, which could be caused by contributions from the direct interface between the two polymer films or an influence of the surface. The observed baseline shift in Δ spectra of about 1° corresponds to a change in the total thickness of about 9 nm. Such an error is too large for thicknesses determined by VIS ellipsometry. Therefore a more likely explanation is that the shift in the baseline originates from slightly overestimated values of the high frequency refractive indices. A decrease of the high frequency refractive indices of about 0.08 would bring a better agreement for the baselines of simulated and experimental Δ spectra. This explanation is reasonable since the high frequency refractive indices, which were used for the simulations of IR ellipsometric spectra, were taken from VIS ellipsometric results. Furthermore, also laterally varying optical constants of the substrate could be the reason for the baseline shift. The measured optical constants of the bare substrate were considered in our simulation, but it has not been ensured that the probed spot for the polymer film and the bare substrate are exactly the same.

### Annealed Double Layer: Mix of PVC and PnBMA on Gold

Figure 4a shows the measured ellipsometric spectra after annealing of the sample for 30 min at 110 °C and the simulated spectra. For simulation of the mixed layer an average value calculated from the optical constants of the single compounds has been used. For calculation of this average value the amounts of the single compounds were weighted according to the ratio of the corresponding thicknesses in the original double layer.

The comparison clearly shows that calculation with a model, which uses a weighted mix of the optical constants of the single polymers, does not work satisfactorily for the description of the annealed film. This behavior is not surprising since conformational changes of the ester groups are expected to occur at annealing, which are frozen by diffusion of PVC molecules into the vicinity of PnBMA molecules.[2] Therefore the optical constants of the mixed films can not be described by a simple averaging of the optical constants of the single compounds and have to be determined separately.

Under the assumption that the annealed double layer (Figure 4) was mixed homogeneously after annealing for 30 min. (for the diffusion kinetic of this material see [17,18]) one could determine the optical constants of the mixed film directly by simulation of the ellipsometric spectra of this sample. The optical constants of the mixed film should allow for simulation of intermediate steps of the mixing. That this principally works is shown in the next part of this section. However, as discussed in a

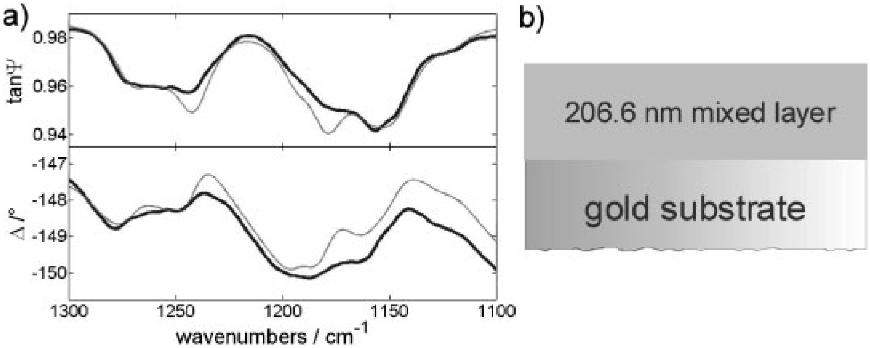

*Figure 4.*
a) Measured (thick black lines) and simulated (thin grey lines) ellipsometric spectra of the double layer after annealing at 110° for 30 min. b) model for simulation.

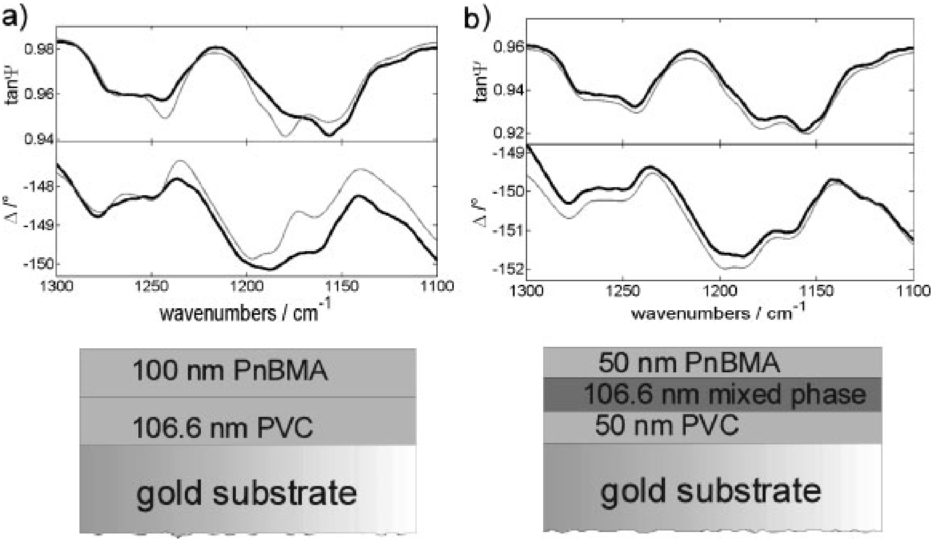

***Figure 5.***
Experimental (black) and simulated (grey) ellipsometric spectra of the double layer annealed for 10 min. a) in a simple double layer model analogue to the one used in Fig. 3. b) three layer model, in which a mixed layer between the original two compounds is assumed. For convenience of comparison the baselines of simulated spectra are shifted.

previous paper[2] the mixing might not be completely homogeneous after 30 min. annealing time.

### Intermediate Step of Mixing: PnBMA/mix/PVC on Gold

Figure 5 shows the measured spectrum of a sample annealed for a shorter time (10 min. at 110 °C) in comparison to two different types of calculations: a) the double layer model as discussed with respect to Figure 3 and b) a three layer model. As input parameter for the optical constants of the mixed film in Figure 5b served the optical constants as determined by a simulation from the measured spectrum of the mixed film in Figure 4.

Compared to Fig. 5a, in Figure 5b a better overall agreement between simulation and experiment can be seen. For PVC (particle)/PnBMA (matrix) blends it was shown that DSC[17] and PALS[18] data can be fitted to gradient profiles in the composition of PnBMA-PVC interface, which are formed due to interdiffusion of the blend components during annealing. The proof of a three phase system consisting of the two pure blend components and a mixed phase was done by DSC for the particle matrix-system.[17] Also in this double layer system such models may fit to the presented data but there is no direct proof of a gradient in the interface composition possible in the moment.

## Conclusion

This study shows that optical simulations can interpret infrared ellipsometric spectra of polymeric multilayers. On the basis of simulations conclusions can be drawn on the macroscopic structure (layer models), but also changes of the microscopic structure, as for example the change of a conformational state of the ester group of the PnBMA molecules can be identified. On one hand simulations are facilitated by the high spectral contrast in the infrared spectral range, which is achieved by the bands of vibrational absorptions. Such specific investigations were not possible in the VIS spectral range since no bands were seen in this spectral range. On the other hand the determination of thicknesses and high frequency refractive indices could be done more accurately from VIS ellipsometric spectra.

Therefore we are working on the application of combined optical simulations of VIS and IR ellipsometric spectra for the analysis of thin film spectra. Currently we focus on ellipsometric studies of thinner films (of below 10 nm thickness) of stimuli responsive mixed polymer brushes.[3]

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