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Infrared Ellipsometric Studies of Mixing in a Thin Double Layer of Poly(*n*-butyl methacrylate)/Poly(vinyl chloride)

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ABSTRACT: Infrared spectroscopic ellipsometry (IRSE), infrared transmission spectroscopy, and the regularized method of deconvolution are applied cooperatively for the analysis of the process of mixing in thin double layers (about 100 nm each) of poly(*n*-butyl methacrylate) (PnBMA) and poly(vinyl chloride) (PVC) on gold. For the first time thin polymeric double layers in the nanometer range and the annealing induced interactions have been investigated by IRSE. Spectral changes in the ellipsometric spectra of thin films are compared to those observed in the infrared absorbance of 5−10 μm thick films of the same polymers. The stabilization of conformational states of side-chain ester groups has been revealed after the annealing process and cooling to room temperature. The formation of hydrogen-bond-type interactions between the PnBMA carbonyl and PVC methine groups in the annealed double layer is found. With increasing annealing time the PnBMA/PVC sample progressively approaches a mixed homogeneous state.

Introduction

The design of thin polymer films and interfaces with defined mechanical and adsorptive properties is of great technological importance. In this field polymer blends have attracted special interest because two or more polymers can be combined in a blend in order to produce new chemical and physical properties.[1−4] Morphology, miscibility, interdiffusion, and interactions at interfaces are key parameters when a polymer blend is studied. An intensively investigated system is the blend of poly(vinyl chloride) (PVC) with poly(methyl methacrylate) (PMMA).[5−9] It has been found that various factors such as the preparation technique, polymer tacticity, and molecular weight may affect the miscibility and morphology of these polymer blends. Recently, efforts have been made to study the mixing process of PVC with other poly(methacrylates) differing in the type of the ester side group.[6,10,11] Dlubek et al.[10,11] studied the transition of a phase-separated system consisting of PVC particles embedded within a poly(*n*-butyl methacrylate) (PnBMA) matrix to a homogeneous mixture due to interdiffusion caused by thermal annealing. However, mixing processes have been investigated so far only in bulky particle/matrix systems or for rather thick double-layer films in the micrometer range. In this work we present a new approach for ellipsometric analysis of such polymer/polymer interdiffusion in the nanometer films. For it, the formation of a homogeneous blend of PVC with PnBMA is investigated, starting from a PnBMA/PVC double layer on gold with a thickness of about 100 nm each. Such a sample can serve as a model system with a defined interface between two polymer compounds.

Various spectroscopic techniques like nuclear magnetic resonance, infrared (IR) and Raman spectroscopy, microscopy, and positron annihilation lifetime spectroscopy (PALS) have been applied for analysis of polymers and their blends.[5−15] Infrared spectroscopy is a very useful standard method for the identification of the molecular structure and the investigation of molecular interactions in polymer blends.[5,12−14] In this work IR ellipsometry[16−18] is applied to analyze the process of interaction at the interface in polymer double layers since it allows to determine layer thickness and it provides a high sensitivity for vibrational bands of thin films. The aim of this work is to identify spectral changes which occur due to the annealing/mixing process in PnBMA/PVC double layers and to correlate them with the molecular structure and intermolecular interactions. For this purpose infrared spectroscopic ellipsometry (IRSE), infrared transmission measurements, and the regularized method of deconvolution[19,20] are used.

In the past decade IR spectroscopic ellipsometry has been used for investigation of thin (<2 μm) layers of various materials.[16−18,21] IRSE enables the determination of optical constants and the analysis of the structure and composition of the samples under study. One advantage of IRSE and as well of other reflection methods is that investigations of nontransparent films or thin films on nontransparent substrates are possible. So far, a few IR ellipsometric studies on thin polymer layers have been published,[18,21] but none on organic double layers and the mixing of different polymers. For interpretation of ellipsometric spectra they have to be simulated in the general case. Layer models are an adequate optical description for many real thin film samples and simulations on the basis of electromagnetic theory; thereby vibrational bands might be considered as Lorentzian oscillators.[18]

When analyzing ellipsometric spectra of films, which consist of polyatomic compounds, the problem may arise that a band in the spectrum is formed by overlapping individual vibrational components. In the case of polymer blends it might be even more problematic because vibrational bands of the different compounds may

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overlap. This situation makes it difficult to determine the actual number of vibrational bands and their corresponding oscillator parameters.

The use of the regularized method of deconvolution[19] allows one to determine frequencies of molecular vibrations in overlapping spectra and moreover to investigate the profile shape of individual bands. In comparison with one other widely used method of derivative spectroscopy, the given method has the advantage that it provides a decrease in the half-widths of bands by maintaining the shape of the resulting profile similar to that of the original band and keeping the integral intensities constant.[20]

For isotropic organic films on metallic substrates in a limited range of thicknesses and under specific optical conditions, the deconvolution method can be directly applied to the measured ellipsometric tan Ψ spectra, which represent the amplitude ratio of p- and s-polarized reflection. In this case (details in section "Results and Discussion") the shape of vibrational bands is comparable to the one in standard absorption spectra. This can be explained by the so-called surface selection rule[22] reducing the dependence of bands in tan Ψ to the p-polarized reflection because only bands for which the transition dipole moments are perpendicular to the surface give a significant contribution. For reflection and tan Ψ spectra in the general case and other kind of substrates this is not necessarily the case, and the band shapes strongly depend on the incidence angle, the optical constants of the substrate, and the anisotropic oscillator parameters of the thin film.

Experimental Part

Materials and Film Preparations. PVC (Aldrich, $\eta = 0.51$, catalog no. 38.929-3) and PnBMA (Polyscience, $\eta = 0.50$, catalog no. 02061) were precipitated from THF solution into methanol before use. The molecular weights M_w/M_n were 63 000/32 000 (g/mol) and $M_w/M_n = 205\,000/103\,000$ (g/mol), and the glass transition temperatures T_g were 84 and 38 °C, respectively (for conditions see refs 10 and 11).

For IR ellipsometric studies thin films of PVC and PnBMA were prepared by spin-coating (1800 rpm, 60 s, room temperature) on gold-coated glass slides (PVC from 1.75 wt % solution in THF/tetrachloroethane (40/60 by weight), PnBMA from 3 wt % solution in di-*n*-butyl ether). The layers were slowly dried in a vacuum with raising temperature up to 60 °C for 1 h. A double-layer system (PnBMA/PVC) was prepared by subsequent coating: first the PVC layer and then the PnBMA layer. The thickness d of the layers was examined by ellipsometry in the visible and infrared range, and the corresponding values d were determined to be as follows: $d = 98.5$ nm (PnBMA), $d = 104.5$ nm (PVC), $d = 207$ nm (PnBMA/PVC). 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. For comparison, a thin (~200 nm) film of the homogeneous PnBMA/PVC blend (1:1 by volume) was prepared from a 3 wt % solution in THF by spin-coating on a gold substrate, which was annealed for further homogenization at 70 °C for 240 min.

Surface morphology of the investigated thin polymer layers before and after annealing was examined by atomic force microscopy (AFM). AFM measurements showed that there were no any surface morphological changes of the samples due to the annealing process.

For IR transmission spectroscopy films of PVC (from THF/tetrachloroethane solution), PnBMA (from di-*n*-butyl ether solution), and a PnBMA/PVC homogeneous mixture (1:1 by volume from THF solution) with thicknesses of 5−10 μm were prepared by casting onto a KBr substrate. The obtained samples were investigated after different annealing steps and at different temperatures. The IR transmission spectra were compared to the IR ellipsometric one.

Spectroscopic Methods. The IR ellipsometric spectra were obtained at room temperature using a photometric ellipsometer attached to a Bruker IFS55 FTIR spectrometer in the 4000−400 cm^{-1} range at a spectral resolution of 2 cm^{-1}. The measurements were performed at the incidence angle of 70°. The procedure of measurement and evaluation of the IR ellipsometric parameters is described elsewhere.[16−18] The IR transmission spectra were recorded on a Bruker IFS55 FTIR spectrometer at a resolution of 2 cm^{-1} averaging 256 scans and transformed afterward to absorbance spectra. The temperature-dependent IR spectra of PnBMA films were measured in a commercial Specac heating cell.

Regularized Method of Deconvolution. The theory of the regularized method of deconvolution has been described in detail elsewhere.[19,20] For different spectral intervals, the deconvolution parameters of the Lorentzian contour half-width (W_L) and the passband value of the deconvolution filter (L) were set as follows: $W_L = 17.0-19.0$ cm^{-1}, $L = 0.12$ cm for the spectral range from 1850 to 1650 cm^{-1}; $W_L = 16.0$ cm^{-1}, $L = 0.12$ cm for the spectral range from 1300 to 1000 cm^{-1}. These values of the deconvolution parameters were chosen to provide the highest resolution enhancement at the given signal-to-noise ratio in the spectra being analyzed. The reliability of the results of mathematical treatment of the experimental ellipsometric spectra was confirmed by the agreement of the deconvolved spectra obtained at slightly differing angles of incidence.

Results and Discussion

IR Ellipsometry on the Thin Single and Double Layers. The annealing-induced interdiffusion between the polymers starting from the PnBMA/PVC double layer (about 100 nm each) should result first in the formation of mixed interlayer and finally, at long annealing times, in a complete homogenization of the originally phase-separated system.[10,11] We analyzed the effects of this process on the IR ellipsometric tan Ψ spectra. The tan Ψ spectra of the original and annealed layers of pure PVC and PnBMA (~100 nm in thickness) served as a kind of reference for interpretation of the double-layer spectra where mixing effects are expected to occur.

Ellipsometric tan Ψ spectra represent, as pointed above, the amplitude ratio of p- and s-polarized reflection. Using optical modeling, we have estimated the amplitudes for the strongest carbonyl stretching band in the tan Ψ spectra of the investigated polymer films on the gold substrates. For a 107 nm thick PnBMA film the amplitude of this band in the s-polarized reflectance spectra is determined to be below 0.6% in comparison to the one in the p-polarized reflectance spectra. Under these limits, for interpretating the tan Ψ spectra the s-polarized electric field components are neglected in the given study, and the shape of the bands is similar to that in the standard absorption spectra. As mentioned above, this approach does not hold in the general case, but it will be still valid for thinner films, higher angles of an incidence, or weaker oscillators. In the present study simple optical layer models have been employed for the determination of the film thickness and refractive indices. In a future work it is planned to consider more specific models such as a gradient within the mixed polymer film.

In our work ellipsometric tan Ψ spectra have been compared to the IR transmission spectra of the same polymers. In doing such a comparison, it should be taken into account that at close values of the frequency

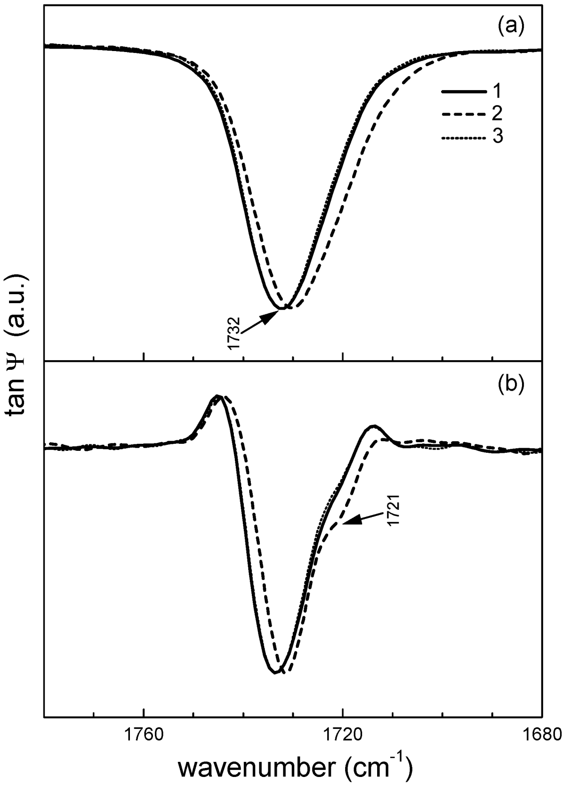

Figure 1. IR ellipsometric tan Ψ spectra in the carbonyl stretching region of the PnBMA/PVC double-layer system before annealing (1) and after annealing at 110 °C for 30 min (2) and of the annealed PnBMA single layer (3): (a) the original spectra; (b) the results of their deconvolution.

positions some differences in the relative intensities and shapes of the bands can be observed. This might be related to the differences in both the sample preparation techniques and the experimantal approaches applied for measuring these spectra.

1800−1650 cm^{-1} Range. In Figure 1a the tan Ψ spectra of the PnBMA single layer and the double layer of PnBMA/PVC before and after annealing are shown in the spectral range of the C=O stretching band of the ester group. When examining changes in the profile shape and peak position of the C=O band, the original experimental and deconvolved spectra have been normalized by the intensity of this band. The tan Ψ spectrum of the untreated PnBMA/PVC double layer is similar to that of the original and annealed PnBMA film. Because the bands of PVC are not expected in this spectral range, this can be explained by the fact that no changes of the carbonyl band of the pure PnBMA single layer occur during the annealing procedure. In contrast, the tan Ψ spectrum of the PnBMA/PVC double-layer system is changed after the thermal treatment, a slight shift of the position, and some asymmetry of the C=O band toward lower frequencies is observed.

1500−900 cm^{-1} Range. In Figure 2, the tan Ψ spectra are shown in the 1500−900 cm^{-1} region. For the pure single polymer films (Figure 2a,b) noticeable changes after annealing are observed only for the PVC. Here a change of band amplitudes at 1435 and 1426 cm^{-1} and an alteration of the broad band near 1256 cm^{-1} are seen. The doublet near 1430 cm^{-1} and the 1256 cm^{-1} band are assigned to the CH_2 and CH deformation modes, respectively.[23,24] It is worth noting that marked differences in the spectra of the PVC thin films before and after annealing are also observed in the conformationally sensitive carbon−chlorine stretching region (700−600 cm^{-1}) (the curve is not shown). The observed spectral variations might be explained by a change in the conformational structure of PVC due to the annealing process.[23,24] Wide-angle X-ray scattering (WAXS) analysis of bulky PVC showed the development of a low degree of crystallinity (about 0.07 ± 0.02) of the originally amorphous material during annealing at 110 °C for 30 min. In the PnBMA/PVC blends and the pure PnBMA no crystallinity at all was observed by WAXS.

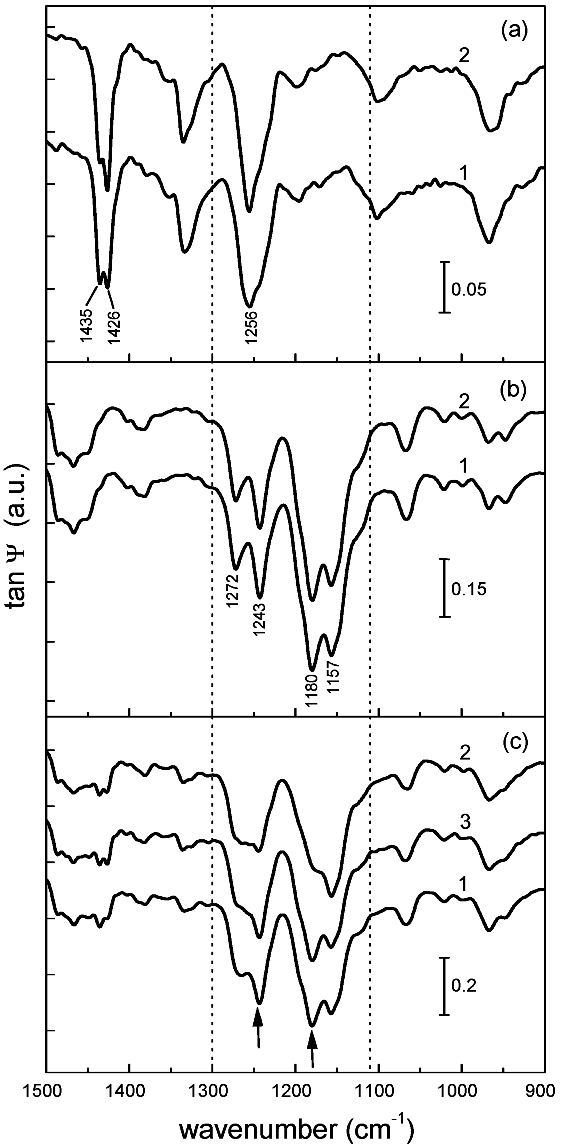

Figure 2. IR ellipsometric tan Ψ spectra in the 1500−900 cm^{-1} region of (a) the PVC film, (b) the PnBMA film, and (c) the PnBMA/PVC double-layer system before annealing (1) and after annealing at 110 °C for 30 min (2). The curve (3) represents the sum of the spectra of annealed PVC and PnBMA films.

For the assignment of the bands in the spectrum of PnBMA in the 1300−1100 cm^{-1} range, we refer to the interpretation recently reported[25] for PMMA, a polymer that differs from PnBMA just in length of the aliphatic alcohol unit in the ester side groups. The bands at 1272 and 1243 cm^{-1} in the spectrum of the PnBMA can be attributed to the C−C−O stretching vibration of the ester group in trans and cis conformations, respectively.[25] The other two most intense bands at 1180 and 1157 cm^{-1} might be related to the C−O−C stretching mode in the ester group and the mixed C−O and skeletal C−C vibrations.[25]

In Figure 2c, the tan Ψ spectra of the PnBMA/PVC double layer and the spectrum obtained by the sum of the spectra of both single polymer films after annealing are shown. The sum spectrum is similar to the spectrum of the untreated double layer. This underlines that no significant interdiffusion processes have been occurred in the double-layer system before the annealing process. After thermal treatment the most pronounced changes are observed for the relative intensities of bands related to the C−C−O stretching vibrations of the ester group at 1272 (trans) and 1243 cm^{-1} (cis) and the intensity of the band near 1180 cm^{-1}.

Deconvolution of the IR Ellipsometric Spectra. 1800−1650 cm^{-1} Range. The results of deconvolution of the carbonyl band (Figure 1b) reveal that the asymmetry observed in the original tan Ψ spectrum of the PnBMA/PVC system after annealing is caused by the appearance of a new band near 1721 cm^{-1}. The observed spectral contour can be best represented as a superposition of the components with Gaussian and Lorentzian profile shapes. The 1721 cm^{-1} band is most likely associated with the vibration of C=O groups influenced by the formation of molecular interactions between PnBMA and PVC molecules in the double layer during thermal annealing. These hydrogen-bond-type interactions involve the carbonyl group of PnBMA and the PVC methine group (Cl−C−H···O=C). The comparatively small frequency shift of the hydrogen-bonded carbonyl band to lower frequencies indicates that the C−H···O interactions are much weaker than typical hydrogen bonds.[26] The existence of such hydrogen bonds has been suggested earlier in spectroscopic studies of PVC/PMMA blends.[6−8]

1300−1100 cm^{-1} Range. The deconvolved tan Ψ spectra of the single polymer films and the double layer of PnBMA/PVC are shown in the 1300−1100 cm^{-1} range in Figure 3. By the use of the deconvolution method, it was possible to reveal the fine structure of the complex bands. The number of extracted bands increases by a factor of about 2 in comparison to the original spectra in Figure 2.

From Figure 3a it follows that the alteration of the profile of the band near 1256 cm^{-1} in the tan Ψ spectrum of annealed PVC film (see Figure 2) is due to a decrease of the low-frequency component of this band at about 1243 cm^{-1}. This component is known to be associated with the deformation vibrations of CH groups in the amorphous regions of PVC.[23]

As a result of deconvolution, it is found that the four bands observed in the original tan Ψ spectrum of PnBMA in this region consist of additional components (Figure 3b). In particular, new bands at 1228, 1196, and 1147 cm^{-1} were revealed.

The vibrational bands in the 1300−1100 cm^{-1} range are associated with combined CO and CC stretching modes in the ester groups and are known to be very sensitive to conformational changes.[25,27,28] Multiplicity of the absorption bands in the given range are attributed to the different conformers of ester groups. Besides, it is expected[27] that several components can correspond to the stretching vibrations of ester groups in one of the possible conformational states. In accordance with the assignment of similar bands in the 1300−1220 cm^{-1} range for PMMA,[25] the peaks at 1272 and 1243 cm^{-1}, as pointed out above, are due to the antisymmetric ν_a(C−C−O) stretching mode of the trans and cis conformations of the ester side group in a PnBMA molecule.

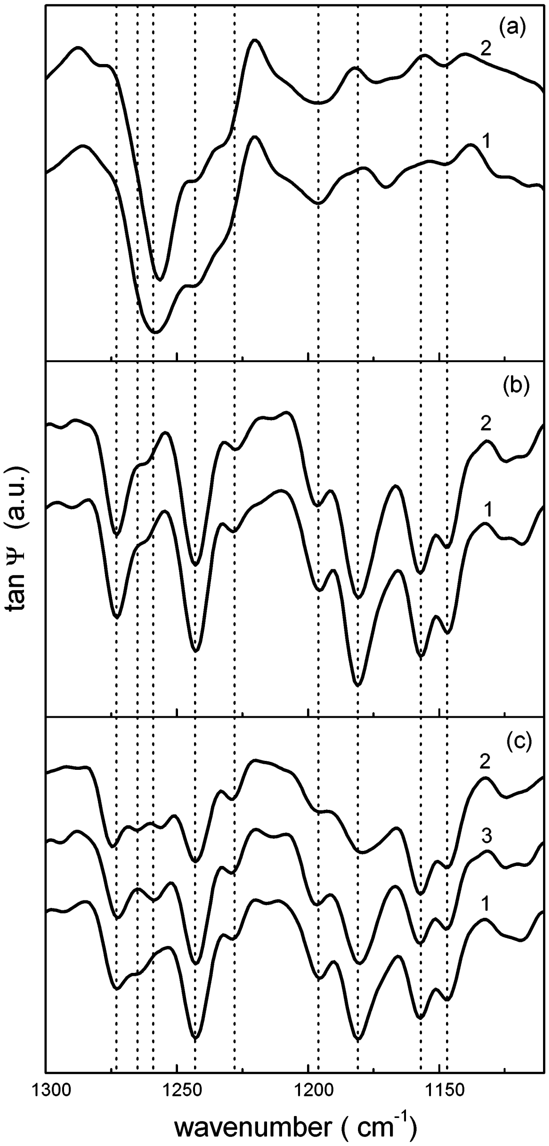

Figure 3. Deconvolved IR ellipsometric tan Ψ spectra in the 1300−1100 cm^{-1} region of (a) the PVC film, (b) the PnBMA film, and (c) the PnBMA/PVC double-layer system before annealing (1) and after annealing at 110 °C for 30 min (2). The curve (3) represents the sum of the spectra of annealed PVC and PnBMA films.

In the 1220−1130 cm^{-1} region antisymmetric ν_a(C−O−C) stretching vibrations in the ester group manifest themselves.[25] Because of the presence of a large side group (OC_4H_9) in the PnBMA molecule in comparison with PMMA, a shift of the frequencies of the ν_a(C−O−C) stretching mode is observed. For PMMA two bands in the above region are associated with different rotational isomers of the ester group.[25] However, there is no overall agreement in the literature with respect to the assignment of certain bands in this range.

An inspection of the deconvolution results in Figure 3c reveals that all the bands of PnBMA also appear in the investigated spectra of the PnBMA/PVC double layer. A contribution of the broad band of PVC at 1256 cm^{-1} results in the considerable broadening of the component near 1272 cm^{-1} in the deconvolved spectrum of the untreated double-layer system. As a result of thermal annealing, the structure of this PVC band

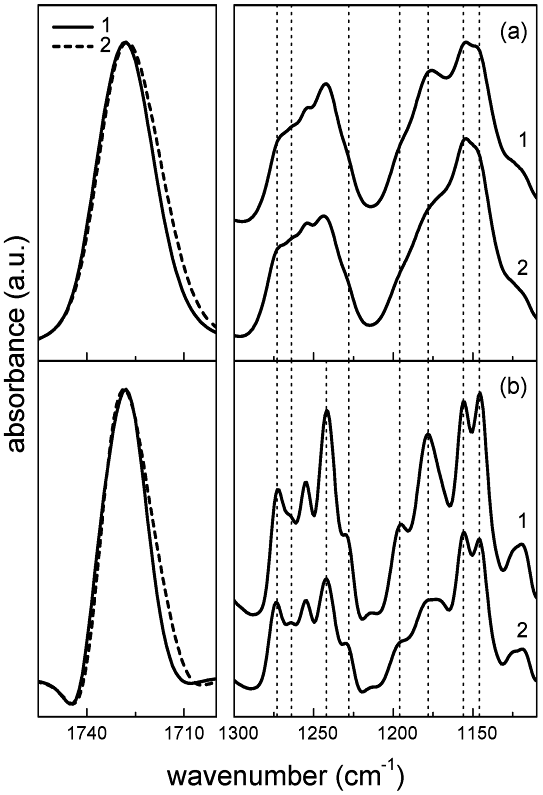

Figure 4. IR absorbance spectra of cast films of the PnBMA/PVC mixture on KBr in the 1750−1700 and 1300−1100 cm^{-1} regions before annealing (1) and after annealing at 110 °C for 100 min (2): (a) the original spectra; (b) the results of their deconvolution.

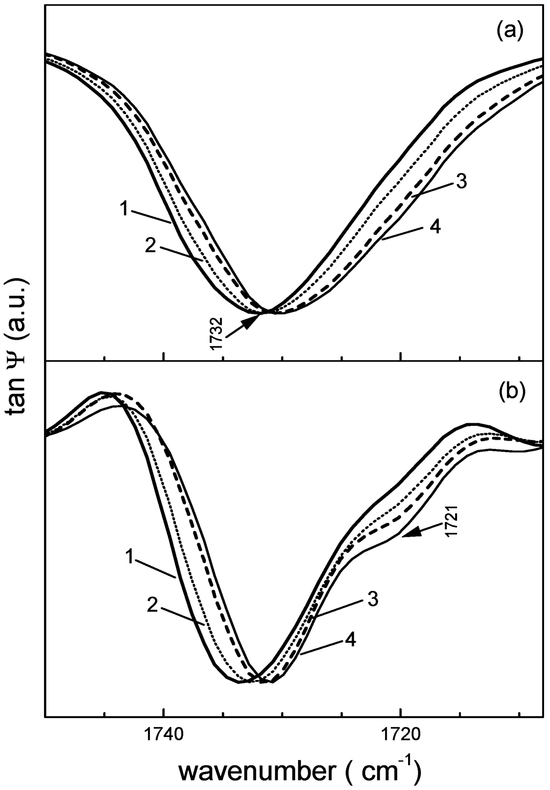

Figure 5. IR ellipsometric tan Ψ spectra in the carbonyl stretching region of the PnBMA/PVC double-layer system before annealing (1), after annealing at 110 °C for 1 min (2) or 30 min (3), and of the single layer of the homogeneous PnBMA/PVC mixture (4): (a) the original spectra; (b) the results of their deconvolution.

changes distinctly (Figure 3a), and it appears well resolved in the sum spectrum in Figure 3c. In the deconvolved spectrum of the PnBMA/PVC double-layer system after annealing (Figure 3c) along with the band of PVC at 1256 cm^{-1}, a component near 1265 cm^{-1} is found. This band is not seen in the sum spectrum of thermally treated PVC and PnBMA single films which indicates that it is connected with the formation of a homogeneously mixed interphase in the annealed PnBMA/PVC system. It might be associated with the C−C−O antisymmetric stretching vibration of the ester group, which is hydrogen-bonded with the PVC methine group.

An annealing induced decrease in relative intensities of the bands near 1243, 1180, and 1196 cm^{-1} together with increase in the relative intensity of the 1157 cm^{-1} band is observed in Figure 3c. In accordance with the assignment of the bands in the range under consideration and the well-known literature data for PMMA,[25,27] the given spectral variations suggest some change of conformational states of the ester side groups. In particular, the decrease of the intensity of the 1243 cm^{-1} band can be interpreted with a smaller amount of cis conformational states of the ester groups in the PnBMA/PVC layer system after annealing.

The original and deconvolved IR absorbance spectra of cast films of the homogeneous PnBMA/PVC mixture before and after annealing are shown in Figure 4. As for the previously discussed double-layer system, some asymmetry of the carbonyl band near 1730 cm^{-1} and the same tendency for band intensity changes in the 1250−1130 cm^{-1} range are found. It is worth noting that the IR absorbance spectrum of the untreated PnBMA/PVC mixture (both original and deconvolved) in the 1300−1100 cm^{-1} region differs somewhat from the IR ellipsometric tan Ψ spectrum of the double layer before annealing, while the corresponding spectra of the annealed samples are similar.

Effect of Different Annealing Times on the PnBMA/PVC Double-Layer System. 1800−1650 cm^{-1} Range. From Figure 5a it can be seen that as the annealing time is raised the profile of the carbonyl band at 1732 cm^{-1} changes progressively at the side of low frequencies. The deconvolution results indicate that this behavior is due to the subsequent increase in the contribution of the low-frequency component near 1721 cm^{-1} to the complex C=O stretching band (Figure 5b). For the PnBMA/PVC double layer the contribution of the C=O band at 1721 cm^{-1} is less compared to the homogeneous mixture since only the mixed interphase contributes to this absorbance. However, the spectra obtained after increasing the annealing times become more and more similar to the spectrum of the homogeneously mixed PnBMA/PVC layer (curve 4 in Figure 5). This observation suggests that the increase of hydrogen-bonded carbonyl groups in the polymer blend is due to the process of interdiffusion, resulting in a growing interphase thickness and volume fraction.

It should be noted that for the investigated PnBMA/PVC double-layer system after annealing, as well as for the homogeneous mixture, the number of C=O groups involved in the hydrogen bonds remains generally small. This fact is consistent with previously reported results about molecular interactions in PVC/PMMA blends.[8]

1300−1100 cm^{-1} Range. A comparison of the original tan Ψ spectra of the PnBMA/PVC double-layer

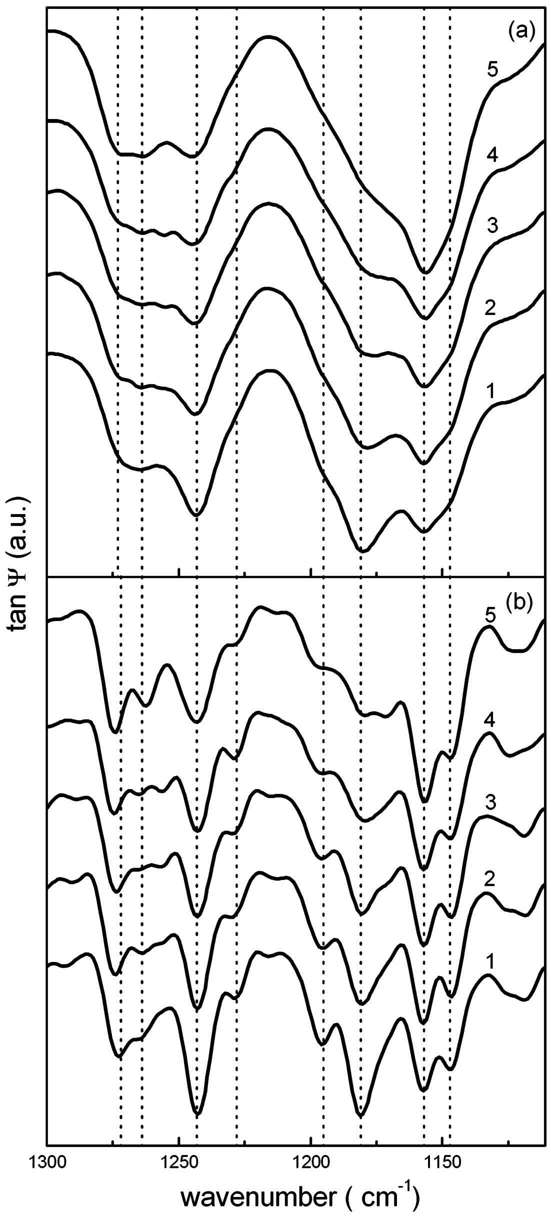

Figure 6. IR ellipsometric tan Ψ spectra in the 1300−1100 cm^{-1} region of the PnBMA/PVC double-layer system before annealing (1), after annealing at 110 °C for 1 min (2), 10 min (3), or 30 min (4), and of the single layer of the homogeneous PnBMA/PVC mixture (5): (a) the original spectra; (b) the results of their deconvolution.

system in the 1300−1100 cm^{-1} range (Figure 6a) indicates that with the increase of the annealing time the relative intensities of the bands near 1243 and 1180 cm^{-1} decrease gradually. Some changes also occur in the higher frequency region 1300−1250 cm^{-1}, where the presence of several components becomes more pronounced. The results of deconvolution reflect a progressive appearance of three bands near 1275, 1265, and 1256 cm^{-1} (Figure 6b). Besides the above-mentioned changes, in the deconvolved spectra one can observe a subsequent decrease of the component near 1196 cm^{-1} in parallel with the increase of the relative intensity of the 1157 cm^{-1} band. As the time of thermal treatment is increased, the spectrum of the PnBMA/PVC system becomes more similar to that of the homogeneous mixture (Figure 6, curve 5), indicating a growing interphase. However, in the case of the homogeneous mixture even smaller band intensities in the 1250−1165 cm^{-1} range along with a higher component at 1157 cm^{-1} are observed. In addition, the band near 1265 cm^{-1} in Figure 6b, which is associated with increased interactions between the blend components, appears better resolved in the deconvolved spectrum of the homogeneous mixture than in the spectrum of the PnBMA/PVC double-layer system annealed for 30 min.

The band of PVC near 1256 cm^{-1} does not appear in the spectrum of the homogeneous mixture. Not observed are the bands near 1426 and 638 cm^{-1}, which are related to the syndiotactic structure of PVC[23,24] (the curves are not shown). This behavior might be explained by the absence of crystalline regions in the homogeneous mixture, as it was found also by WAXS analysis.

In summary it is found that with increasing annealing time interdiffusion occurs in the double-layer system. However, the comparison with the homogeneous mixture shows that the process of mutual diffusion of the two polymer blend components is not completed in the applied annealing time. Instead, a multiphase PnBMA/PVC system consisting of layers with the original polymer components and their mixed interlayer is formed.

Dlubek et al. evaluated the thickness of the mixed interlayers in dependence on the annealing time for the same polymers but in the particle/matrix system using PALS[10] and differential scanning calorimetry[11] data. When annealing for 10 min, the thickness of the layer effected by mutual diffusion was about 60 nm and after 30 min about 140 nm. However, they have found that the diffusion concentration profile and therefore the interfacial one are not symmetric since the diffusion coefficients are concentration-dependent. PVC molecules may faster diffuse into the high mobile PnBMA phase than vice versa. It is worth noting that the diffusion behavior of the curved interface may differ from that of the plane interface, and the values given in the above works can be only roughly extended for the double-layer system under study, even if identical polymers have been used.

Temperature-Dependent IR Transmission Spectroscopy of Pure PnBMA. In the previous sections it has been found that annealing of the thin PnBMA/PVC double layers on gold causes spectral changes. In the 1300−1100 cm^{-1} range the variations of the relative intensities of the bands without any shifts of their positions occur. The most obvious spectral differences in the given region were explained by changes in the conformational states of ester groups in PnBMA molecules. To get a deeper insight into the origin of such behavior, IR transmission measurements of cast films of pure PnBMA have been performed at elevated temperatures.

In Figure 7, IR absorbance spectra of PnBMA films at different elevated temperatures and after cooling to 30 °C are shown. It can be seen that the initial spectrum at 30 °C undergoes some changes when the temperature is raised, but after cooling again the 30 °C spectrum is quite close to the original one. This might be explained by a reversible change of the conformational states of ester groups.

A decrease in the relative intensities of the bands in the 1250−1165 cm^{-1} range is observed when heating pure PnBMA cast films up to 200 °C. The changes are reversible and very similar to the changes observed in the spectra of the PnBMA/PVC double-layer system after annealing at 110 °C for 30 min and cooling. This

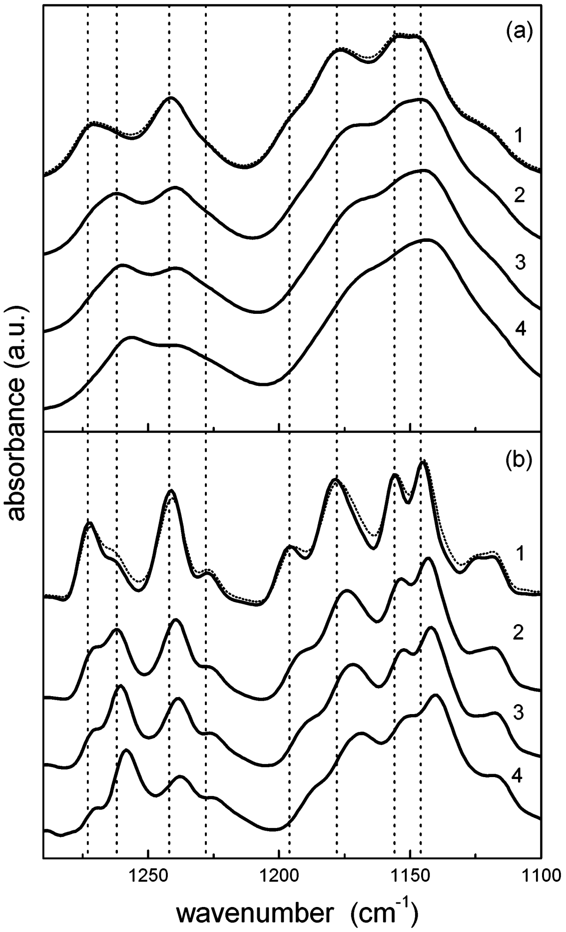

Figure 7. IR absorbance spectra of cast PnBMA films on KBr in the 1300−1100 cm^{-1} region at 30 °C (1), 110 °C (2), 150 °C (3), and 200 °C (4) and after cooling again to 30 °C (· · ·): (a) the original spectra; (b) the results of their deconvolution.

indicates that the high-temperature population distributions of conformational states of ester groups have been stabilized in the double-layer system by the presence of PVC molecules. For the PnBMA/PVC layer system after annealing, as compared to the PnBMA films at elevated temperatures, some spectral differences are observed. In particular, the bands do not change their frequencies, and also a pronounced redistribution of the relative intensities of the components at 1156 and 1146 cm^{-1} occurs.

Conclusions

As a result of using IRSE and the regularized method of deconvolution, we determined characteristic spectral changes caused by the formation of a molecular mixed phase in the PnBMA/PVC double-layer system, which can be used for analytical purposes. A spectroscopic manifestation of hydrogen-bond-type intermolecular interactions in the PnBMA/PVC blend was found. Increasing annealing time leads to a better mixing in the studied double-layer system, which is in accordance with the increase in the fraction of hydrogen-bonded carbonyl groups. The process of interdiffusion in the investigated PnBMA/PVC system is accompanied by a change of the conformational states of the ester groups in PnBMA molecules due to interactions with the PVC molecules. The content of cis conformational states therewith decreases.

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