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The effects of specific interactions on the surface structure and composition of miscible blends of poly(vinyl alcohol) and poly(N-vinyl-2-pyrrolidone)

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Poly(vinyl alcohol) (PVAL)/poly(N-vinyl-2-pyrrolidone) (PVP) blends were studied by differential scanning calorimetry (d.s.c.), Fourier transform infrared spectroscopy (*FT*i.r.), and X-ray photoelectron spectroscopy (XPS). A single glass transition temperature (T_g) was observed for all PVAL/PVP blends, suggesting that PVAL/PVP blends are miscible within the compositions considered. The specific interaction (hydrogen bonding) between PVAL and PVP was investigated by d.s.c. and *FT*i.r. The surface chemical composition of the blends was studied by XPS. The XPS result showed that PVAL is enriched on the surface of the PVAL/PVP blends in spite of the formation of intermolecular hydrogen bonds between the C=O in PVP and the OH in PVAL. The intermolecular hydrogen bonds also induce a change of 0.3–0.4 eV in the O1s binding energy difference between the oxygen atoms in the carbonyl and hydroxyl groups. It can be concluded that the formation of the intermolecular hydrogen bonds is a major factor for the miscibility of the PVAL/PVP blends in the bulk and that the difference in the surface energy between PVAL and PVP is the dominant factor that controls the surface composition of the blends. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: hydrogen bond; polymer blend; surface chemical composition)

INTRODUCTION

The chemical and physical properties of polymer surfaces are important in determining the suitability of polymers in many applications such as adhesion, biomaterials, protective coatings, friction and wear, composites, microelectronics devices, and thin-film technology. The surface properties depend critically upon the chemical and physical characteristics of the polymer materials. These important characteristics include the polymer chain structure, such as the relative length of the blocks, flexibility of the blocks[1] and their sequence length distribution[2–4], the bond orientations with respect to the surface, and the depth distribution of various constituents. In order to obtain the desirable surface properties, a thorough understanding of the relationship between bulk and surface properties of polymers is necessary.

Generally, the bulk and surface compositions of polymer blends are not the same even though they are miscible in the bulk. The significant enrichment of the low surface energy component at the surface of polymer blends is frequently noted[5–9]. Based on the work of Schmidt and Binder[10], Jones and Kramer[11] have derived a simple expression to predict the surface composition of a miscible blend at equilibrium. Their result indicates that a difference of 1 $\mathrm{mJm^{-2}}$ in the surface free energy of the blend components can lead to an enrichment of the lower surface energy component at the polymer blend surface.

In recent years, considerable progress has been made in recognition of the importance of specific interactions in the phase behaviour of polymer blends. One of the most important intermolecular interactions is the hydrogen bond between a proton donor and a proton acceptor. The hydrogen bonding has been shown to be responsible for miscibility of many polymer blends[12,13].

X-ray photoelectron spectroscopy (XPS) has been applied to study the surface composition and structure of polymer blends[5–16] and copolymers[2–18]. Because the binding energy of a core level electron depends on its chemical environment within the molecule, the binding energy information can be used to study the specific interaction between polymers at the surface. Only a very few studies have been made to investigate the effects of the specific interaction, such as the hydrogen bond, on the surface composition and structure of miscible polymer blends. In a recent study, Goh *et al.*[9] have applied XPS to study the ionic interaction between sulfonated polystyrene and poly(styrene-co-4-vinylpyridine). Shifts in the binding energy of the N1s and S2p core levels were detected. In addition, their results indicate that poly(styrene-co-4-vinylpyridine), being the lower surface energy component, still segregates to the surface although the ionic interaction between these two polymers is strong. The blends of poly(vinyl alcohol) (PVAL)/poly(N-vinyl-2-pyrrolidone) (PVP) have been shown to be miscible by d.s.c. and *FT*i.r.[19–22]. Their results indicate that miscibility in these blends is a result of the formation of hydrogen bonds

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between the C=O groups in PVP and the OH groups in PVAL. In this study, the effects of the hydrogen bond on the surface composition and structure of these miscible polymer blends were investigated by XPS.

EXPERIMENT

PVAL ($\overline{M}_w = 115\,000$, 99.7 wt% hydrolysed) and PVP ($\overline{M}_w = 360\,000$) were purchased from Scientific Polymer Product, Inc. (Ontario, New York) and were used as received. Blends were prepared by mixing different amounts of the two homopolymers in purified water. The solutions with 2 wt% of polymers were poured into PTFE Petri dishes. The samples were vacuum desiccated for 48 h before any analysis.

XPS spectra were recorded on a PHI 5600 multitechnique system equipped with an Al monochromatic X-ray source. A pass energy of 11.75 eV was used. All core level spectra were referenced to the C1s neutral carbon peak at 284.8 eV. XPS samples were prepared by spin-casting a solution of 0.5 wt% polymer blend on a Si wafer. In order to study the migration of the polymer chains, two-layer polymer films were prepared by spin-casting a thin layer of PVAL film (water was used as the solvent) on a Si wafer and then spin-casting another layer of PVP film (methanol was used as the solvent) on the top of the PVAL film. These samples were annealed at different temperatures (25, 90 and 120°C) for 24 h in a nitrogen environment.

The d.s.c. measurements were performed with a TA 2910 DSC at a heating rate of 20°C/min from 273°K to 523°K. Two heating and cooling cycles were obtained. During the experiment, a continuous N_2 purge at 20 cm^3/min was used. The T_g was taken as the onset of the change in slope from the plot of heat capacity as function of temperature in the second cycle.

RESULTS AND DISCUSSION

d.s.c. analyses

All PVAL/PVP blend films are optically clear. A single T_g is observed for all PVAL/PVP blends, suggesting miscibility[19–22]. A summary of the d.s.c. results for the PVAL/PVP blends is presented in *Table 1*. A melting peak is observed in the d.s.c. scans for the PVAL/PVP blends containing ≥ 50 wt% PVAL, and its value decreases with decreasing PVP content. The depression of the melting point of a crystallisable component in a miscible blend has been used to determine the Flory–Huggins interaction parameter χ. Painter *et al.*[23] have modified the Nishi–Wang equation to account for the effect of strong specific interaction. However, due to the lack of data necessary for this model, the simple Nishi–Wang model[24], which describes the melting point depression of a crystalline polymer (component 2) due to the presence of a miscible diluent (component 1), is used. When the miscible diluent is a polymer, the entropy of mixing becomes negligible and the melting point depression will be largely enthalpic in nature. The resulting equation for the melting depression is

Table 1 Glass transition temperatures and melting points of PVAL, PVP and their blends

PVAL (wt%)	T_g (°C)	T_m (°C)
0	181.5	—
20	156.0	—
30	142.0	—
40	117.1	—
60	100.8	207.6
70	104.5	211.1
80	90.1	213.4
100	79.9	215.9

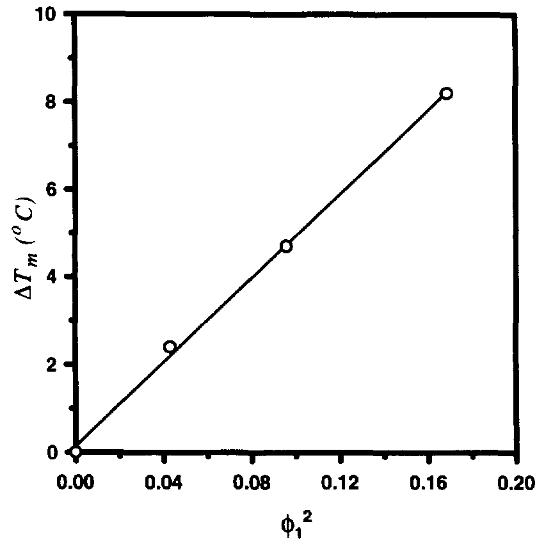


Figure 1 Plot of the melting point depression as a function of the square of the volume fraction of PVP

$$\Delta T_m = -T_m^o\left(\frac{V_2B}{\Delta H_2}\right)\phi_1^2 \qquad (1)$$

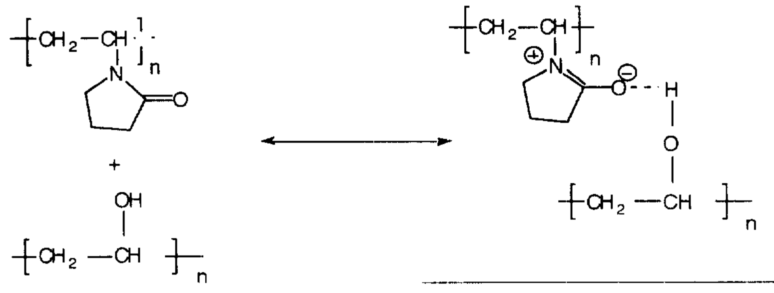
where ΔT_m is the equilibrium melting point depression, T_m^o is the melting point of the pure crystalline polymer (component 2), V_2 and ΔH_2 are the molar volume of the repeating unit and heat of fusion per mole of repeating unit, respectively for component 2, and ϕ_1 is the volume fraction of component 1. The term B is related to the Flory–Huggins interaction parameter χ by

$$\chi = \frac{BV_1}{RT_m} \qquad (2)$$

where R is the gas constant, V_1 is the molar volume of the repeat unit for component 1, and T_m is the melting point of the blend. *Figure 1* shows a plot of the observed melting point depression as a function of the square of the volume fraction of PVP. A least-squares fit of the data yields a straight line intersecting the vertical axis near zero with a slope of 56.84. Using the values $T_m^o = 215.8$°C, $\rho_1 = 1.21$ g/cm^3 (density of component 1), $\rho_2 = 1.34$ g/cm^3, $V_1 = 92.0$ cm^3/mol, $V_2 = 32.8$ cm^3/mol, and $\Delta H_2 = 1.6$ kcal/mol[22], the calculated value of B is -5.67 cal/cm^3. The calculated value of χ is -0.52 at 230°C, which is similar to the values published in the literature[21,22]. This large negative value is characteristic of very strong intermolecular interactions.

FTi.r. results

The interactions between two polymers can be deduced from the shifts of the vibration frequencies of the groups involved in the hydrogen bonding. If two polymers are compatible, then the infrared spectra obtained for the blends should include band shifts and broadening when compared to the infrared spectra of the homopolymers. In the PVAL/PVP blends, these changes are due to the formation of hydrogen bonds between the hydroxyl and carbonyl groups, as shown in the following.

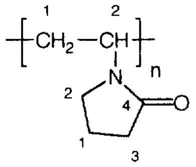


As suggested by Ping *et al.*[22], the carbonyl band shifts towards lower frequencies as the PVP content increases, and the hydrogen-bonded hydroxyl group shifts towards higher frequencies upon blending with PVP. When hydrogen bonds of pure PVAL are replaced by interpolymer hydrogen bonds in the blend, the hydroxyl absorption band shifts to higher frequencies indicating that the hydrogen bonds formed in the blend are weaker than those in the pure PVAL.

In order to investigate the effect of temperature on the formation of intermolecular hydrogen bonds, special samples were prepared by depositing a PVP film on a PVAL film. *Figure 2* shows the carbonyl stretch region of these samples pressed at different temperatures. After annealing for 24 h at 90 and 120°C (above the glass transition temperature of PVAL), a second band is observed at lower frequencies. This band is assigned to the hydrogen-bonded PVP carbonyl groups, which are formed by mutual diffusion of the polymers due to higher chain mobility at elevated temperatures.

Surface analysis

Thin films of the homopolymers and the PVAL/PVP blends are prepared by spin-casting a polymer from a polymer blend solution on a Si wafer. The samples were analysed by XPS. The spectra were obtained at a take-off angle of 45° (the sampling depth was estimated to be about 45 Å using an attenuation length of 22 Å). *Figure 3* shows the C1s spectra for the homopolymers (PVP and PVAL) and their blends. The C1s spectrum for PVP is shown to comprise four peaks by curve fitting. The positions of these four peaks are determined to be at 284.8, 285.2, 286.1 and 287.7 eV, as shown in *Table 2*. Peaks 1–4 correspond to carbon atoms in PVP with different atomic environments, as shown below.



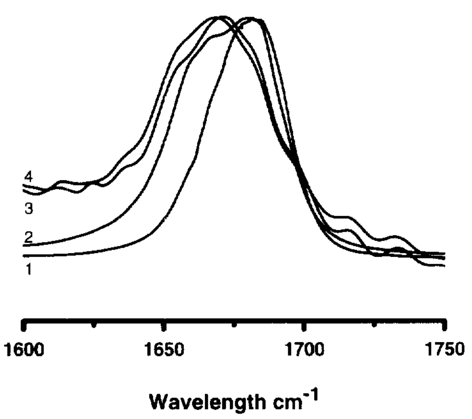


Figure 2 Carbonyl stretching region of PVAL and PVP for the films pressed at different temperatures for 24 h: (a) PVP homopolymer; (b) two-layer (PVAL and PVP) films annealed at 25°C; (c) same as (b) except at 90°C; and (d) same as (b) except at 120°C

These results are very similar to the literature values[25]. The C1s spectrum for PVAL is shown to comprise two peaks, which are determined to be at 248.8 and 286.3 eV. The high binding energy peak corresponds to the carbon atom adjacent to the OH group. The C1s spectra for the blends, as shown in *Figure 3*, can be resolved into five peaks, which all correspond to various carbon atoms in the two polymers. However, the C1s spectra for the blends are slightly too complicated for extracting detailed chemical information for the formation of hydrogen bonding between the C=O and OH groups. The O1s spectra for the homopolymers and the blends are shown in *Figure 4*. A small peak at approximately 533 eV in the O1s spectrum for PVP is believed to be caused by retained water[25]. The binding energies for the O1s and N1s core levels for the homopolymers were determined and the results are summarised in *Table 3*. The O1s binding energy difference between the C=O and OH groups (ΔO1s) in these two homopolymers is 1.4 eV, which agrees well with the results of Briggs[25]. The O1s spectra for the blends are much broader than those of the homopolymers because of the presence of the two types of oxygen (C=O and OH). When the C=O groups in PVP and the OH groups in PVAL form intermolecular hydrogen bonds, the O1s binding energy of the C=O groups increases because of the electron transfer from the C=O groups to the OH groups; while, the O1s binding energy of the OH groups decreases due to the

Table 2 Core levels for C1s, N1s and O1s for the PVAL and PVP homopolymers

Polymer		C1s (eV)				N1s (eV)	O1s (eV)	$I_{N/C}$	$I_{O/C}$
		1	2	3	4				
PVP	BE	284.8	285.2	286.1	287.7	399.7	531.2	0.159	0.153
	FWHM	1.2	1.1	1.2	1.1	1.2	1.3		
PVAL	BE	284.8	286.3				532.6		
	FWHM	1.1	1.1				1.4		0.473

Table 3 Binding energies of the O1s core levels and the O1s binding energy difference between the oxygen atoms in the PVAL and PVP

PVAL	N1s (eV)	O1s (eV)		Difference of the O1s
Surface volume fraction	N	CHOH	NC=O	Δ O1s (eV)
PVAL		532.6		1.4
0.979		532.6	531.2	1.4
0.953		532.6	531.5	1.1
0.886	399.9	532.7	531.5	1.2
0.731	400.0	532.5	531.5	1.0
0.585	399.9	532.6	531.5	1.1
0.422	399.8	532.5	531.5	1.0
0.392	399.8	532.5	531.5	1.0
PVP	399.7		531.2	

increase in the electron density. As a result, the binding energy differences between the oxygen in the C=O groups and the oxygen in the OH groups of the blends are smaller than that of the homopolymers. The value of the ΔO1s decreases as the PVAL surface volume fraction increases, as shown in *Table 3*. These XPS results suggest that the intermolecular hydrogen bonds between C=O and OH groups can cause a change of 0.3–0.4 eV in the O1s binding energy difference between these two functional groups. It is interesting to note that the values for ΔO1s are quite large even though the surface volume fraction of PVP is very small. The increase in the N1s binding energy due to the formation of the hydrogen bonds is approximately 0.2–0.3 eV. Shifts in the binding energy in polymer blends with strong specific interactions have been observed by Goh *et al.*[9]. Their XPS study on the ionic interactions between sulfonated polystyrene and poly(styrene-co-4-vinylpyridine) indicates that the binding energy of N1s core level of the pyridinium ions (protonated pyridine), formed by the ionic interactions, is about 2.5 eV higher than that of the pyridine. The presence of hydrogen bonding in the PVP/PVAL blends detected by the binding energy measurements is in agreement with the d.s.c. and *FT*i.r. results.

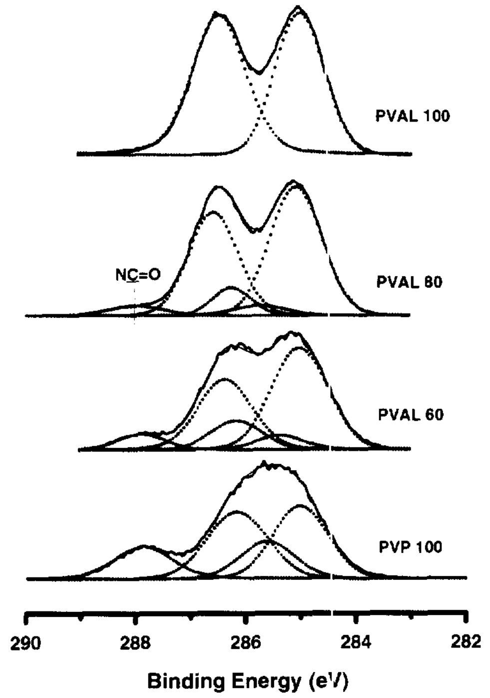


Figure 3 C1s core level spectra for PVAL and PVP homopolymers and their blends

The surface composition of PVP and PVAL blends was determined by measuring the C/N peak area ratios with the PVP homopolymer as the standard. The results are summarised in *Table 4*. It is apparent from *Table 4* that all PVAL/PVP blends display a surface excess of PVAL. *Figure 5* is a plot of the PVAL surface volume fraction *versus* PVAL bulk volume fraction. The PVAL surface volume fraction is not linear with respect to the PVAL bulk volume fraction. The surface segregation of PVAL is caused by the difference in the surface energy of the two homopolymers. The solid surface tensions of semicrystalline PVAL and PVP homopolymers were reported to be 37.0 and 53.6 dynes/cm,[26] respectively. Even though the PVAL/PVP blends are completely miscible in the bulk because of the formation of hydrogen bonds between PVAL and PVP, the lower surface energy component (PVAL) still segregates to the surface of blends. These results clearly show that the reduction in the free energy as a result of surface segregation of the lower surface energy component can overcome the increase in enthalpy due to breaking up some intermolecular hydrogen bonds between PVAL and

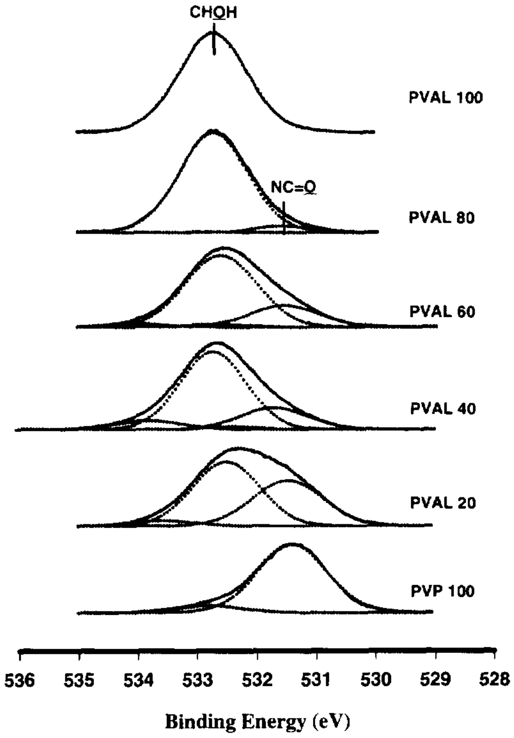


Figure 4 O1s core level spectra for PVAL and PVP homopolymers and their blends

Table 4 PVAL surface composition calculated from C/N peak area ratios

PVAL bulk		PVAL surface
wt %	Volume fraction	Volume fraction
0.0	0.000	0.000
5.0	0.049	0.087
10.0	0.097	0.190
20.0	0.196	0.392
28.4	0.278	0.422
35.0	0.343	0.463
40.0	0.392	0.585
60.0	0.589	0.731
80.0	0.792	0.886
90.0	0.895	0.953
95.0	0.947	0.979
100.0	1.000	1.000

Table 5 PVAL surface compositions calculated from the C/N peak area ratios

Annealing	PVAL surface volume fraction	
temperature (°C)	PVP 0.5 wt % solution	PVP 0.2 wt% solution
25	0.000	0.479
90	0.057	—
120	0.068	0.591

PVP. It is important to point out that the surface chemical composition of solution-cast thin films is strongly influenced by their morphologies[27]. An increase in surface roughness will result when the concentration of the crystallisable component is high. *Figure 6* shows an AFM image of a film sample obtained by spin-casting a solution of 0.5 wt% polymer blend (the weight ratio of PVAL to PVP = 80:20) on a Si wafer and a cross-sectional profile along a line marked in the image. These results indicate that the surface of the sample containing a high concentration of PVAL is relatively smooth—the maximum variation is less than 2 nm. Hence, it is reasonable to assume that the surface roughness of these samples will not have a significant effect on the surface chemical composition.

Effects of thermal history

To study the migration of the lower surface energy component of a polymer blend, two-layer film samples were prepared. The samples were prepared by first spin-casting a layer of PVAL on a Si wafer and then spin-casting another layer of PVP film on the top of the PVAL layer. The thickness of the PVP films was varied by using 0.2 and 0.5 wt% PVP solutions in methanol. The surface composition of these samples after annealing at different temperatures for 24 h was analysed by XPS. *Table 5* gives the results of surface compositions calculated from the C/N peak area ratios. For the samples with a thinner top layer of PVP, a large amount of PVAL was detected on the surface even at low temperatures. This may be a result of an incomplete coverage by the thin film. For the sample, with a thicker layer of PVP film on the top the PVAL film, annealed at 25°C, no PVAL was detected at the surface because at this low temperature, PVAL cannot diffuse through the thick PVP layer. However, more PVAL was detected on the surface of the samples when they are annealed at high temperatures. These results indicate that even at the temperatures (120°C) below the T_g of PVP, segments of the PVAL chains can diffuse into the glass state of the PVP layer and segregate to the surface in spite of the strong intermolecular hydrogen bonds between PVAL and PVP in the bulk.

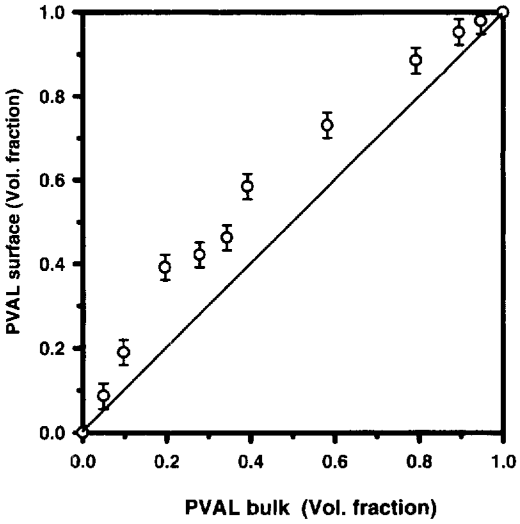


Figure 5 PVAL surface volume fraction *versus* PVAL bulk volume fraction

CONCLUSIONS

The hydrogen bonds between the C=O in PVP and the OH groups in PVAL induce a change of 0.3–0.4 eV in the O1s binding energy difference between these two functional groups. XPS results show that the surface of the PVAL/PVP blends is enriched with the lower surface energy component (PVAL) in order to minimise the surface free energy. In the bulk of the PVAL/PVP blends, the hydrogen bonding between PVAL and PVP is the cause for miscibility; however, its effect is still not strong enough to prevent surface segregation of PVAL.

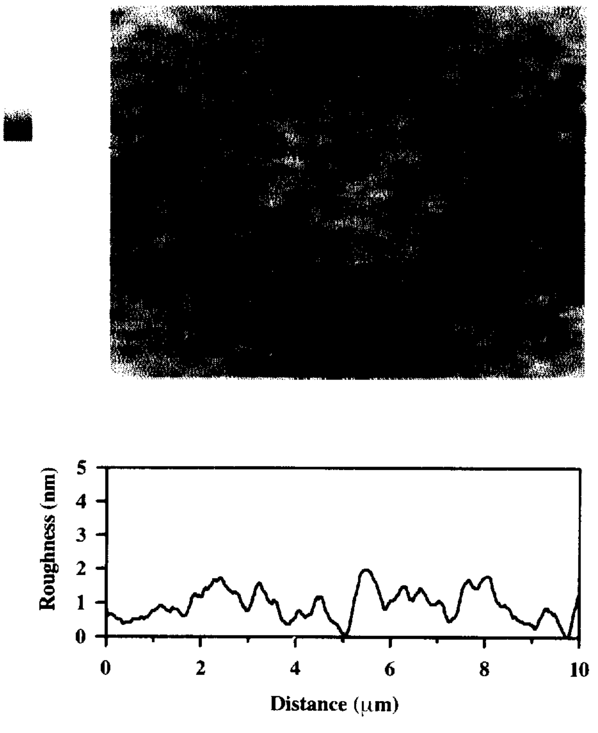


Figure 6 AFM image of a film sample obtained by spin-casting a solution of 0.5 wt% polymer blend (the weight ratio of PVAL to PVP = 80:20) on a Si wafer and a cross-sectional profile along a line marked in the image

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