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Miscibility and Interactions in Blends and Complexes of Poly(*N*-acryloyl-*N*′-methylpiperazine) with Poly(*p*-vinylphenol)

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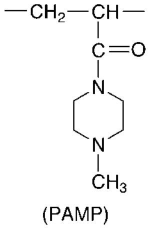
ABSTRACT: A low-molecular-weight poly(*N*-acryloyl-*N*′-methylpiperazine) (PAMP-L) forms miscible blends with poly(*p*-vinylphenol) (PVPh) while a high-molecular-weight PAMP-H forms complexes with PVPh in ethanol solutions. The glass-transition temperatures of all the blends and complexes are higher than those predicted by a linear additivity rule. The specific interactions between PAMP and PVPh were studied by Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). FTIR shows that the hydroxyl group of PVPh interacts with both the carbonyl oxygen and the amide nitrogen of PAMP as shown by the development of a low-frequency and high-frequency carbonyl band in each blend and complex. The amide nitrogen and amine nitrogen of PAMP are discernible by XPS. Both types of nitrogens are involved in interactions with PVPh as shown by the development of two additional high-binding-energy N 1s peaks in each blend or complex. All three types of interacting sites of PAMP interact with the hydroxyl groups of PVPh.

Introduction

For the formation of a miscible blend from two dissimilar polymers, the two polymers must possess suitable interacting sites in order to achieve specific interactions. For a polymer possessing two or more types of interacting sites, it is important to know which is the preferred interacting site. For example, poly(dimethyl itaconate) (PDMI) possesses two −COO− groups in each segment. However, it is the −COO− group further away from the main chain that interacts with the hydroxyl group of poly(*p*-vinylphenol) (PVPh).[1] The interaction between an *N*-methylated polyamide and a polystyrene ionomer is through the carbonyl oxygen atom but not the nitrogen atom.[2]

There are three possible hydrogen-bond interacting sites in each segment of poly(*N*-acryloyl-*N*′-methylpiperazine) (PAMP): the carbonyl oxygen atom and the two nitrogen atoms. It appears that the study of specific interactions in blends of PAMP can be quite complicated. The involvement of the carbonyl group in hydrogen-bonding interactions can be monitored by Fourier transform infrared (FTIR) spectroscopy.[3] The development of a low-frequency carbonyl band in a blend indicates the existence of hydrogen-bonding interactions through the oxygen atom. Our recent works have shown that X-ray photoelectron spectroscopy (XPS) is useful to study specific interactions in blends of nitrogen-containing polymers.[4−10] When the chemical environment of nitrogen in a blend is perturbed because of specific interactions, the development of a new peak with a higher binding energy (BE) can be observed in the XPS spectrum. The two different nitrogen atoms in PAMP are discernible by XPS. Therefore, a combination of FTIR and XPS will be useful in studying specific interactions in blends of PAMP. This paper reports the miscibility and specific interactions in PAMP/PVPh blends and complexes.



(PAMP)

Experimental Section

Materials. *N*-Methylpiperazine (Aldrich Chemical Co., Inc), acryloyl chloride (Fluka), and triethylamine (Mallinckrodt Chemical, Inc.) were used as received. PVPh (M_w = 22 000) was supplied by Polysciences, Inc.

Synthesis of PAMP. The monomer, *N*-acryloyl-*N*′-methylpiperazine, was prepared by reacting acryloyl chloride with *N*-methylpiperazine in the presence of triethylamine.[11]

Two batches of PAMP were prepared by free-radical polymerization in bulk using azobis(isobutyronitrile) (AIBN) as the initiator. The first batch was prepared at 60 °C for 24 h using 0.1 wt % AIBN, producing a high-molecular-weight sample, PAMP-H. The second batch was prepared at 70 °C for 24 h using 2.0 wt % AIBN to give a low-molecular-weight sample, PAMP-L. The two PAMP samples were purified by two dissolution/precipitation cycles using 1,4-dioxane as the solvent and *n*-hexane as the nonsolvent. The number- and weight-average molecular weights of PAMP-H and PAMP-L as determined by gel permeation chromatography are 64 000 and 95 000, and 2000 and 3700, respectively.

Preparation of Blends and Complexes. PVPh, PAMP-H, and PAMP-L were separately dissolved in ethanol (1% w/v). Precipitates formed immediately upon mixing the ethanol solutions of PVPh and PAMP-H. After 1 h of continuous stirring, polymer complexes in the form of precipitates were isolated by centrifugation and washed with ethanol. The complexes were then dried in vacuo at 90 °C for 2 weeks. The ratio of the amount of dried complex to the total amount of the two polymers in the initial solutions gives the yield of the complex. The nitrogen contents of various complexes were

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Table 1. Characteristics of PAMP-H/PVPh Complexes

complex	0.38AMP0.62VP	0.41AMP0.59VP	0.47AMP0.53VP
feed composition[a]	0.25	0.44	0.65
bulk composition[a]	0.38	0.41	0.47
surface composition[a]	0.33	0.36	0.40
yield (%)	54	62	50
T_g (°C)	193	187	181
α	1.24	1.24	1.33
N (amide) 1s peaks (eV)	399.7, 400.5	399.7, 400.5	399.7, 400.5
N (amine) 1s peaks (eV)	399.0, 400.0	399.0, 400.0	399.0, 400.1
fraction of the high-BE peak of N (amide) 1s	0.49	0.42	0.40
fraction of the high-BE peak of N (amine) 1s	0.62	0.68	0.54

[a] Mole fraction of PAMP-H.

determined by elemental analysis using a Perkin-Elmer 2400 elemental analyzer.

The mixing of the ethanol solutions of PVPh and PAMP-L did not lead to precipitation. The mixed solution was allowed to evaporate to dryness. The cast blends were similarly dried in vacuo at 90 °C for 2 weeks. All the dried blends and complexes were stored in a desiccator to prevent moisture absorption. The blends and complexes are designated as *x*AMP*y*VP where *x* and *y* are the mole fractions of PAMP and PVPh, respectively.

The bulk compositions of various blends and complexes were calculated from their nitrogen contents as determined by elemental analysis using a Perkin-Elmer 2400 elemental analyzer. The surface compositions of the blends and complexes were determined by XPS measurements based on the nitrogen/oxygen peak−area ratio after correction with appropriate sensitivity factors.

T_g Measurements. The glass-transition temperatures (T_g's) of various samples were measured with a TA Instruments 2920 differential scanning calorimeter (DSC) using a heating rate of 20 °C/min. Each sample was subjected to several heating/cooling cycles to obtain reproducible T_g values. The initial onset of the change of slope in the DSC curve is taken to be the T_g. The T_g's of PVPh, PAMP-H, and PAMP-L are 154, 83, and 77 °C, respectively.

FTIR Characterization. FTIR spectra were recorded on a Bio-Rad 165 FTIR spectrophotometer. Sixty-four scans were signal-averaged at a resolution of 2 cm^{-1}. Spectra were recorded at 150 °C using a SPECAC high-temperature cell, equipped with an automatic temperature controller, which was mounted in the spectrophotometer. Blend samples for FTIR analysis were prepared by casting the ethanol solutions onto KBr disks followed by drying in vacuo at 90 °C for 2 weeks. Complex samples were prepared by grinding the dry complex with KBr powder and compressing the mixture to form disks.

XPS Measurements. XPS measurements were made on a VG ESCALAB MKII spectrometer equipped with a Mg Kα X-ray source (1253.6 eV photons) and a hemispherical energy analyzer. Various blends and complexes were ground to fine powders and were then mounted on standard sample studs by means of a double-sided adhesive tape. The X-ray source was run at 12 kV and 10 mA, and a pass energy of 20 eV was used in the analyzer. The pressure in the analysis chamber was maintained at 10^{-8} mbar or lower during measurements. All core-level spectra were referenced to the C1s neutral carbon peak at 284.6 eV and obtained at a takeoff angle of 75° to the sample surface. Each spectrum was curve-fitted using the XPSPEAK95 Version 3.1 software. In the curve fitting, the widths (fwhm) of Gaussian peaks were maintained constant for all components in a particular spectrum.

Results and Discussion

General Characteristics of Blends and Complexes. All the ethanol-cast PAMP-L/PVPh blends were transparent and each showed a single T_g, indicating miscibility. As shown in Figure 1, the T_g−composition curve for PAMP-L/PVPh blends can be fitted by the Kwei equation:[12,13]

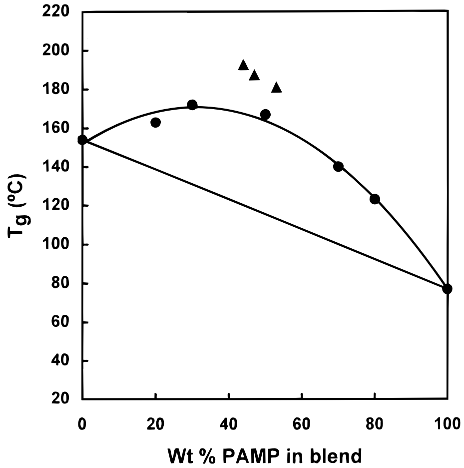


Figure 1. T_g−composition curve of PAMP-L/PVPh blends (●) and PAMP-H/PVPh complexes (▲).

$$T_g\ (\text{blend}) = [(w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2)] + qw_1w_2$$

where *k* and *q* are fitting constants. The curve in Figure 1 was drawn using *k* and *q* values of 1 and 180, respectively. The T_g values of the blends show large positive deviations from the expected T_g values based on a linear additivity rule.

PAMP-H formed complexes with PVPh in ethanol solutions over the entire feed composition. The characteristics of the complexes are shown in Table 1. The T_g values of PAMP-H/PVPh complexes are in the range of 181−193 °C, which are higher than those of the PAMP-L/PVPh blends (Figure 1). It is generally observed that a complex shows a larger positive deviation in its T_g value than a blend because of the more intimate contact in the complex.[14,15]

The formation of complexes requires the chain lengths of interacting polymers to exceed a certain critical value.[16−18] A long polymer chain allows more cooperative interaction, facilitating complex formation. Apparently, the chain length of PAMP-L is not long enough to induce precipitation. It should be noted that the absence of precipitation for the PAMP-L/PVPh system is due to the smaller number of cooperative interactions between the two polymers rather than the absence of interactions. Interactions between different polymer chains in solution can be revealed by viscosity and laser light-scattering studies.[19−23] For example, Zhou et al.[23] studied the miscibility and complexation between modified polystyrene [PS(OH)] and poly(ϵ-caprolactone) (PCL). When the hydroxyl content of PS(OH) is 8 mol %, the reduced viscosities of PS(OH)/PCL solutions in toluene show large negative deviations from the linear additive values, indicating the presence of interactions between

Table 2. Characteristics of PAMP-L/PVPh Blends

blend	1[a]	2[a]	3[a]	4[a]	5[a]
bulk composition[b]	0.20	0.30	0.50	0.70	0.80
bulk composition[c]	0.16	0.23	0.44	0.65	0.76
surface composition[c]		0.18	0.37	0.59	
T_g (°C)	163	172	167	140	123
α		1.36	1.34	1.29	
N (amide) 1s peaks (eV)		399.7, 400.5	399.7, 400.5	399.7, 400.6	
N (amine) 1s peaks (eV)		399.0, 400.0	399.0, 400.1	399.0, 400.0	
fraction of the high-BE peak of N (amide) 1s		0.35	0.42	0.43	
fraction of the high-BE peak of N (amine) 1s		0.58	0.45	0.44	

[a] Blend 1, 0.16AMP0.84VP; blend 2, 0.23AMP0.77VP; blend 3, 0.44AMP0.56VP; blend 4, 0.65AMP0.35VP; blend 5, 0.76AMP0.24VP. [b] Weight fraction of PAMP-L. [c] Mole fraction of PAMP-L.

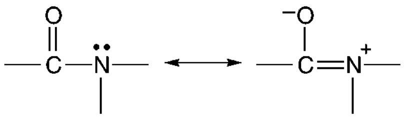
the two polymers. However, precipitation occurs when the hydroxyl content of PS(OH) is increased to 17 mol %. In the present work, the precipitates obtained from PAMP-H and PVPh are called complexes while the films obtained from evaporation of the PAMP-L/PVPh solutions are called blends. Such a terminology for complexes and blends was also adopted by other researchers.[18,24−26]

It has been observed that the composition of an interpolymer complex depends on its feed composition.[5,7,14,15,24,26−28] Similarly, the composition of the PAMP-H/PVPh complex also depends on the feed composition as shown in Table 1. Furthermore, all the PAMP-H/PVPh complexes and PAMP-L/PVPh blends show a surface enrichment of PVPh (Tables 1 and 2). Pan and Prest[29] suggested the use of the relative enrichment factor (α) to compare surface enrichment. In the present case, α is expressed by

$$\alpha = \frac{(S_{\mathrm{PVPh}}/B_{\mathrm{PVPh}})}{(S_{\mathrm{PAMP}}/B_{\mathrm{PAMP}})}$$

where S_i and B_i are the surface composition and bulk composition of polymer i in the blend or complex, respectively. The α values of various blends and complexes as shown in Tables 1 and 2 are around 1.3, showing that the extents of enrichment of PVPh in the surface regions of all the complexes and blends are about the same.

FTIR Characterization. The amide group of PAMP may be described as a hybrid of two resonance structures with two possible hydrogen-bond interacting sites, the amide nitrogen and the carbonyl oxygen, at which interactions can occur with proton-donating polymers:[2,30,31]



The absorption band of this amide group, the so-called amide I, is a combination of the C═O and C−N stretching modes.[31] If the interaction is through the oxygen, the stretching energy of the C═O bond should decrease and the infrared absorption for the carbonyl group will shift to a lower frequency. However, if the interaction is through the lone-pair electrons on the nitrogen atom, the frequency of the carbonyl band should increase.[30] Figure 2 shows the carbonyl stretching region of the FTIR spectra for PAMP-H and its complexes with PVPh. PAMP-H has a strong carbonyl stretching absorption at 1640 cm^{-1}. It is of interest to note the presence of a new band at 1653 cm^{-1} in the complexes, which indicates that the hydroxyl group of PVPh interacts with the lone-pair electrons on the nitrogen atom of the amide group through hydrogen bonding. There is no previous report on such a phenomenon for blends and complexes of tertiary amide polymers. On the other hand, there is another band located at 1625 cm^{-1}, showing the presence of hydrogen-bonding interaction between the hydroxyl groups of PVPh and the carbonyl oxygen of PAMP. However, this peak is not distinct because of the interference of the benzene ring stretching band. This phenomenon suggests that the hydroxyl groups of PVPh interact with both hydrogen-bond interacting sites in the amide groups of PAMP.

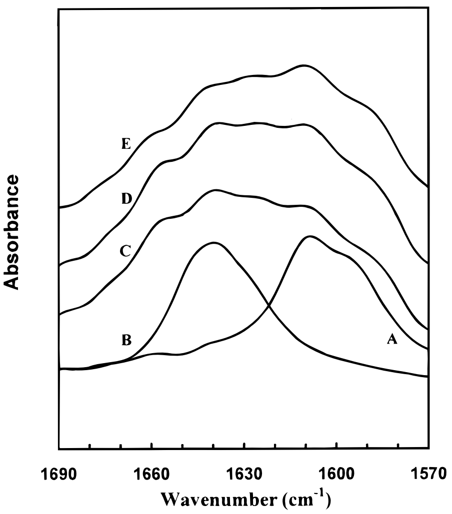


Figure 2. FTIR spectra, recorded at 150 °C, of the carbonyl region of PAMP-H, PVPh, and PAMP-H/PVPh complexes: (A) PVPh; (B) PAMP-H; (C) 0.47AMP0.53VP; (D) 0.41AMP0.59VP; (E) 0.38AMP0.62VP.

Figure 3 shows the FTIR spectra of the PAMP-L/PVPh blends. The spectra show essentially the same features as those observed in Figure 2, showing that the hydroxyl groups of PVPh are also interacting with both the carbonyl oxygen atoms and the amide nitrogen atoms of PAMP-L.

Figure 4 shows the infrared spectra of the PAMP-H/PVPh complexes in the hydroxyl region at 150 °C. PVPh shows a band centered at 3525 cm^{-1}, attributed to free hydroxyl groups, and a broad band centered at 3369 cm^{-1}, which represents a broad distribution of self-associated hydroxyl groups. The center of the broad hydrogen-bonded hydroxyl band of the complex shifts from 3369 to 3340 cm^{-1}, showing that the intermolecular hydrogen-bonding interactions are stronger than the self-association of PVPh. In addition, the intensity of the free hydroxyl band at 3525 cm^{-1} of the complexes is reduced significantly, indicating that a large number

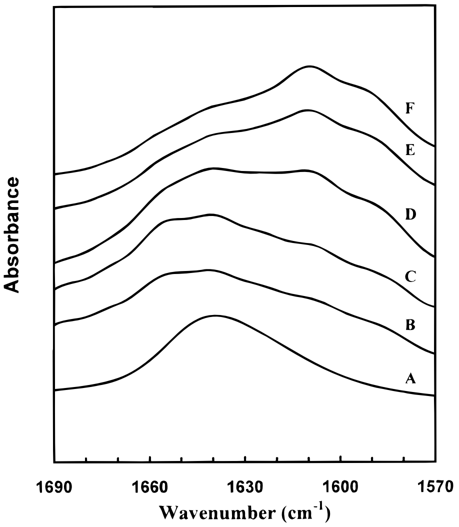


Figure 3. FTIR spectra, recorded at 150 °C, of the carbonyl region of PAMP-L and PAMP-L/PVPh blends: (A) PAMP-L; (B) 0.16AMP0.84VP; (C) 0.23AMP0.77VP; (D) 0.44AMP0.56VP; (E) 0.65AMP0.35VP; (F) 0.76AMP0.24VP.

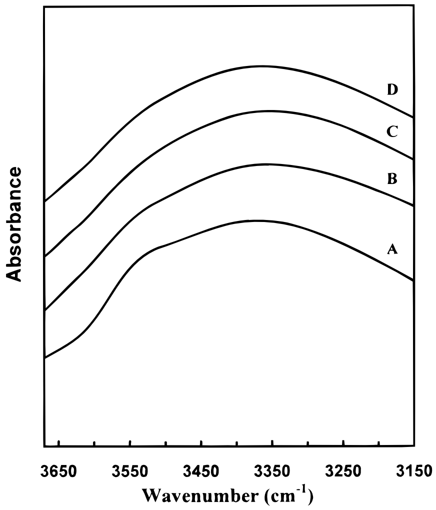


Figure 4. FTIR spectra, recorded at 150 °C, of the hydroxyl region of PAMP-H/PVPh complexes: (A) PVPh; (B) 0.38AMP0.62VP; (C) 0.41AMP0.59VP; (D) 0.47AMP0.53VP.

of free hydroxyl groups are involved in intermolecular association with PAMP.

Figure 5 shows the infrared spectra of PAMP-L/PVPh blends in the hydroxyl region at 150 °C. The center of the broad hydrogen-bonded hydroxyl band also shifts from 3369 to 3340 cm^{-1}. The free hydroxyl band at 3525 cm^{-1} of the blend becomes less intense with increasing PAMP-L content.

XPS Characterization. Figure 6 shows the N1s spectra of PAMP-L and the three blends. For PAMP-L, the N1s peak can be deconvoluted into two component peaks. The peak at 399.0 eV is attributed to the amine nitrogen and the peak at 399.7 eV is attributed to the amide nitrogen. The assignment is based on the consideration that the amide nitrogen bears a partial positive charge because of the resonance structure, and therefore its BE is larger. The N1s peaks of the blends are broader and asymmetric, and each peak can be deconvoluted into four component peaks, with two remaining at 399.0 and 399.7 eV. The presence of two new high-BE N1s peaks is evidenced in the spectra of all the blends, indicating that both types of nitrogen in

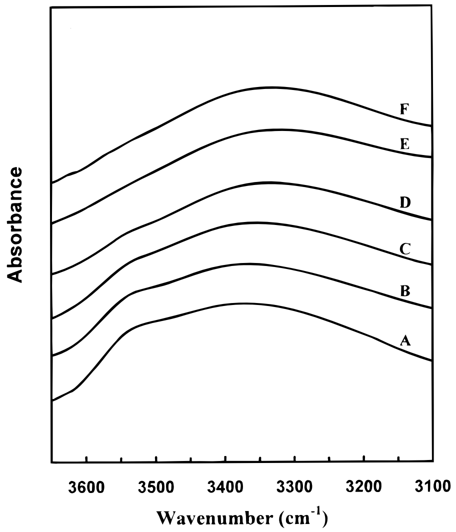


Figure 5. FTIR spectra, recorded at 150 °C, of the hydroxyl region of PAMP-L/PVPh blends: (A) PVPh; (B) 0.16AMP0.84VP; (C) 0.23AMP0.77VP; (D) 0.44AMP0.56VP; (E) 0.65AMP0.35VP; (F) 0.76AMP0.24VP.

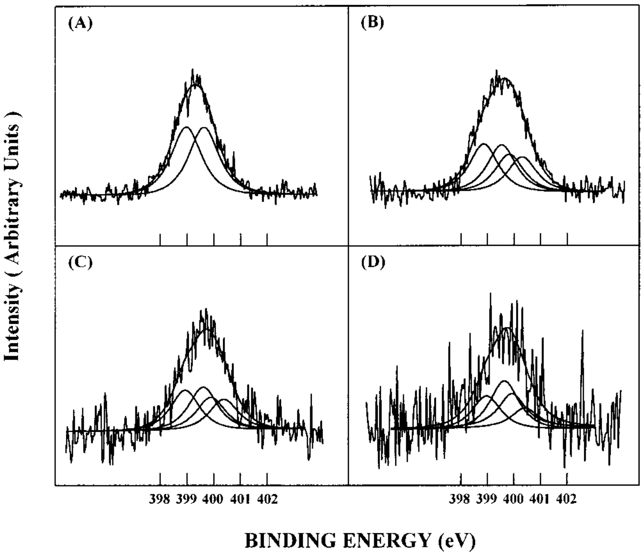


Figure 6. N1s spectra of PAMP-L/PVPh blends: (A) PAMP-L; (B) 0.65AMP0.35VP; (C) 0.44AMP0.56VP; (D) 0.23AMP0.77VP.

PAMP-H interact with PVPh. The BE values of the two high-BE N1s peaks are 400.0 and 400.5 eV. The former peak, with a BE value 1.0 eV higher than 399.0 eV, is attributed to the interaction between the tertiary amine nitrogen and the hydroxyl group of PVPh. The BE value of the latter peak is 0.8 eV higher than 399.7 eV and it is attributed to the interaction involving the amide nitrogen. Our recent studies on complexes of poly(vinylpyridine) have shown that a shift of about 1.0 eV for N1s is observed for complexes involving hydrogen-bonding interactions.[6,7] It is suggested from Figure 6 that tertiary amine nitrogen interacts more strongly with PVPh than the amide nitrogen does, since the tertiary amine nitrogen shows a larger BE shift. The different BE shifts of the two nitrogens arise from their different electronic environments. Since the amide nitrogen bears a partial positive charge, its interaction with the hydroxyl group is not as intense as compared to that of the neutral amine nitrogen.

The fractions of the amine nitrogen and amide nitrogen of PAMP involved in hydrogen-bonding inter-

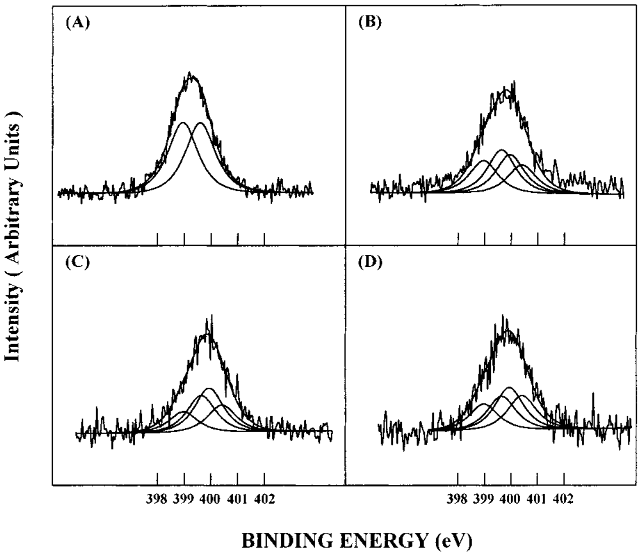


Figure 7. N1s spectra of PAMP-H/PVPh complexes: (A) PAMP-H; (B) 0.47AMP0.53VP; (C) 0.41AMP0.59VP; (D) 0.38AMP0.62VP.

actions can be estimated from the area of the high-BE N1s peaks. As shown in Tables 1 and 2, more amine nitrogen atoms undergo hydrogen-bonding interactions with PVPh than amide nitrogen atoms.

Figure 7 shows the N1s spectra of PAMP-H and the three complexes. Similarly, the N (amine) 1s peak at 399.0 eV shows a shift of 1.0 eV after complexation, and the N (amide) 1s peak at 399.7 eV shows a shift of 0.8 eV.

Conclusions

PAMP-L is miscible with PVPh while PAMP-H forms complexes with PVPh in ethanol. FTIR and XPS studies have shown that all the three interacting sites of PAMP are involved in hydrogen-bonding interactions with the hydroxyl groups of PVPh. To our knowledge, there have been no previous reports that a polymer interacts with another polymer through three interacting sites.

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