

Miscibility and Specific Interactions in Blends of Poly(4-vinylphenol-co-methyl methacrylate)/Poly(styrene-co-4-vinylpyridine)

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ABSTRACT: The miscibility and phase behavior of poly(4-vinylphenol-co-methyl methacrylate) (PVPhMMA50) containing 50% of methyl methacrylate with random copolymers of poly(styrene-co-4-vinylpyridine) (PS4VPy) containing 5, 15, 30, 40, and 100% of 4-vinylpyridine, respectively, were investigated by differential scanning calorimetry, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). It was shown that for a composition of 4-vinylpyridine less than 30%, all blends of PVPhMMA50/PS4VPy are immiscible, characterized by the apparition of two glass transitions (T_g) over their entire composition range. However, above this composition, a single T_g has been observed in all the blends of PVPhMMA50 and PS4VPy. When the amount of vinylpyridine exceeds to 40% in PS4VPy, the obtained T_g s of PVPhMMA50/PS4VPy blends were found to be signifi-

cantly higher than those observed for each individual component of the mixture indicating that these blends are able to form interpolymer complexes. FTIR analysis reveals the existence of preferential specific interactions via hydrogen bonding between the hydroxyl and pyridyl groups and intensifies when the amount of 4VPy is increased in PS4VPy copolymers. Furthermore, the quantitative FTIR study carried out for PVPhMMA50/PS4VPy blends was also performed for the vinylphenol and vinylpyridine functional groups. These results were also confirmed by SEM study. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: differential scanning calorimetry; fourier transform infrared spectroscopy; interpolymer complexes

INTRODUCTION

The research of new polymer materials with improved properties has received considerable attention in both the academic and industrial points of view. However, it has been established that in most cases the polymer blends are immiscible due to their high molecular weight and the weak or the unfavorable interactions between the polymers.^{1–3} Unfortunately, this fact is, in general, undesirable due to their poor mechanical properties and restricts their use in a wide range of industrial applications.

In this way, the polymer blending is an attractive approach to obtain new polymeric materials with large scale properties. It has been demonstrated to be an effective alternative in achieving enhanced ma-

terial properties such as better processability, lowered cost, and so on. Thermodynamically, the miscibility of polymer blends is mainly dependent on the value of mixing enthalpy, because the contribution of mixing entropy is negligible. In general, to obtain a miscible blend system, it is usually necessary to guarantee that favorable specific interactions exist between the components or to the sufficient intramolecular repulsions between comonomers of the blends.^{4–7}

It has been reported that two polymers, which initially form an immiscible system, could be enhancing their compatibility by introducing the complementary chemical structures capable to establish specific interactions between their chains. For this reason, several methods have been proposed. Among them, the introduction of specific interactions, within two dissimilar constituents by copolymerization has been widely used. Karasz et al. have been suggested that blends of poly(2,6-dimethylphenylene oxide) (PPO) and random copolymers of styrene (S) and methyl methacrylate (MMA) were found to be miscible up to a copolymer content to 18 wt % of MMA. Above this critical MMA content,

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the blends of PPO/PSMMA exhibit two T_g s occurring the phase separation.⁸ Some years ago, Paul and Barlow have enumerated several cases of miscible binary blends involving copolymers when their corresponding homopolymers are not similarly miscible.⁷ In this context, several types of specific interactions have been reported. Among them, the hydrogen bonding plays an important role in enhancing the physical and thermodynamical properties of polymer materials.^{9–12}

Poly(vinylphenol-*co*-methyl methacrylate) (PVPh-MMA50) is an interesting synthetic copolymer with a broad range of industrial applications. Their copolymers are mainly used in electronics for solder resists, etching resists, presensitized printing plates, coatings, and adhesives. In addition, due to their high gas barrier properties, they are used in food packaging products.¹² Poly(styrene-*co*-4-vinylpyridine) (PS4VPy) is also an amorphous polymer. The styrene groups of this copolymer have poor capacity to form interactions with polar groups. For PS4VPy/PVPhMMA50 blends, the interactions between styrene groups and hydroxyl or carbonyl groups are weak (mainly of the van der Waals type). Furthermore, the pyridine groups are the only chemical groups available to develop strong interactions (hydrogen bond type) with hydroxyl groups.

In this article, the phase behavior and miscibility of blends of poly(vinylphenol-*co*-methyl methacrylate) (PVPhMMA50) containing 50% in mol of MMA with a range of PS4VPy random copolymers will be investigated. The miscibility of these binary blends will be studied by means of differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). First, we examined in detail by DSC the phase behavior and miscibility of these blends according to their glass transition temperatures (T_g s). Moreover, the effect of incorporating the pyridine groups into polystyrene (PS) chains on the phase behavior of different blends will be described. Second, the possible specific interactions were studied qualitatively and quantitatively by FTIR. Third, the relationship between the observed phase behaviors of blends as determined by DSC, the formation of hydrogen bonding explored by FTIR and SEM is also discussed.

EXPERIMENTAL

Materials

Poly(4-vinylphenol-*co*-methyl methacrylate) (PVPhMMA50) containing 50 mol % of MMA was purchased from Aldrich and used as received.

PS4VPy containing 5, 15, 30, 40, or 50 mol % of 4-vinylpyridine (PS4VP05, PS4VP15, PS4VP30,

TABLE I
Characteristics of Polymers Used in This Work

Polymers	M_w	M_w/M_n	T_g (°C)
PS4VP05	103,000	1.80	105
PS4VP15	134,000	1.60	109.5
PS4VP30	98,500	1.54	114
PS4VP40	143,000	1.77	116.5
PS4VP50	130,000	1.38	122
P4VP	60,000	1.73	145.3
PVPhMMA50	150,000	1.84	135.8

PS4VP40, and PS4VP) of different styrene contents were synthesized by solution-free radical polymerization at 60°C using azo-bis-isbutyronitrile as initiator and chloroform as solvent. The different copolymers were purified by reprecipitation from chloroform solution into an excess of heptane and dried under vacuum for several days. The 4-vinylpyridine contents in the PS4VP copolymers were determined by elemental analysis and ¹H NMR. The molecular weights of these copolymers were determined by GPC relative to PS standard. The polydispersities were found in the range of 1.6–1.8.

Blends of PS4VPy with poly(vinylphenol-*co*-methyl methacrylate) (PVPh-*co*-PMMA) were prepared by solution casting from tetrahydrofuran (THF) solution. The glass transition temperatures of pure polymers and of their binary blends were measured with a Perkin Elmer DSC PYRIS 1 equipped with an intracooler. All T_g measurements were carried out at a heating rate of 20°C/min under nitrogen flow and the T_g value was taken as the midpoint of the transition of the second scan.

FTIR measurement was recorded on a Nicolet Avatar 560 FTIR spectrometer, and 32 scans were collected with a spectral resolution of 2 cm⁻¹. Infrared spectrum of the polymer blends was obtained by using the conventional KBr disk method. The films were prepared by casting in THF onto a KBr disk. All the samples were dried to constant weight in vacuum oven at 60°C for several days to evaporate the solvent slowly. The different samples of PVPhMMA50/PS4VP blends were fractured cryogenically, and their scanning electron micrograms were taken with a HITACHI S2700 scanning electron microscope. The characteristics of these polymers are given in Table I.

RESULTS AND DISCUSSION

DSC Study

The transition behaviors observed with the polymers have long been used as a basic criterion in the study of the miscibility of polymer blends. Thus, the study of glass transitions can provide important information about the physical state and morphology of

these blends. These phenomena can also provide important information about the possible relaxations that occur at the segments level during the transition.¹³

Furthermore, many techniques can be used to investigate the phase behavior and miscibility of polymer blends. For this purpose and owing to their simplicity and speed, thermal analyses, spectroscopy, and microscopic methods are regularly used. These techniques offer information about the miscibility in the different range scales. Hence, the observation of single glass transition for polymer blends determined by DSC makes evident the homogeneity of the blend on the scale of 20–30 nm. Then, it is reported that the NMR spectroscopy can prove this homogeneity at a molecular scale.^{14,15} Therefore, it has been concluded that the FTIR is proven to be a most powerful for the characterization of specific interactions and phase behavior of polymer blends through the observed variation of spectroscopic vibration bands, known as frequency shift.

The DSC appears to be one of the most fundamental techniques used to study these phenomena. In general, the DSC is the most convenient method to elucidate the miscibility of polymer blends. It is at once simple and offers rapid results and fundamental characteristic of the physical state, morphology, and orientation of the chains. For all these advantages, we have therefore adopted this technique to study our systems. It has been established that the observation of a single glass temperature transition (T_g) between those of the pure constituents is indicative of their miscibility, whereas the detection of the two T_g s corresponding to the pure constituents, respectively, indicating their immiscibility.^{16–18}

It is well known that the binary polymeric system of poly(4-vinylphenol) (PVPh) poly(methyl methacrylate) (PMMA) and their copolymers (PVPhMMA) with PS have been found to be immiscible over the whole range of compositions and accessible temperatures.¹⁹ This behavior has been attributed to the repulsive interactions that occurred between unlike species of the blend, which lead to their immiscibility. On the other hand, the immiscibility can be avoided if there are specific interactions between the components of the blend, rendering the mixing enthalpy negative and the blend thermodynamically stable.

In order to improve the miscibility of the mixture of PS with PVPhMMA50, we have first carried out a chemical modification of PS by introducing 5 mol % of 4-vinylpyridine into PS by copolymerization. The thermograms corresponding to PS4VP05, PVPhMMA50, and their blends of different compositions are displayed in Figure 1. Two glass transition temperatures are observed with each composition similar to those of the pure constituents PS4VP05 and

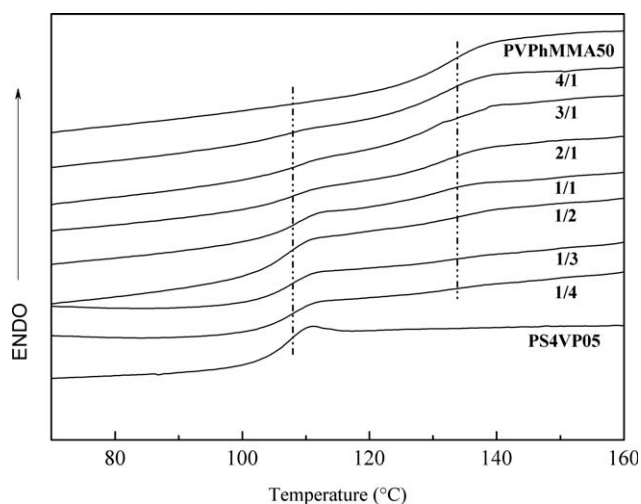


Figure 1 DSC thermograms of PVPhMMA50/PS4VP05 blends.

PVPhMMA50, respectively. As it can be seen the introduction of 5 mol % of vinylpyridine into PS, considered as good proton acceptor, into PS is not sufficient to achieve their miscibility. Although the strength of specific interactions that occurred between the hydroxyl groups of vinylphenol (VPh) and the 4VP nitrogen atom of pyridine are relatively stronger, the amount of intramolecular interactions: hydroxyl–carbonyl and hydroxyl–hydroxyl in PVPhMMA50 is obviously very important. Therefore, we can state that the enhancing of the attractive interactions between comonomers 4-vinylphenol and 4-vinylpyridine may be not sufficient to provide the miscibility between the blends of PS4VP05 and PVPhMMA50.

Hence, when the composition of 4-vinylpyridine in PS4VP increases above 20 % mol, the single glass transition temperature (T_g) has been observed for each composition. This is indicative for their miscibility attributed to the existence of specific interactions intermolecular. The T_g -composition traces were also showed a positive deviation from the additivity rule. Moreover, when the amount of vinylpyridine exceeds to 40% in PS4VP, the obtained T_g s of PS4VPy/PVPhMMA50 blends were found to be significantly higher than those observed for each individual component of the mixture as occurs in PS4VP40, PS4VP50, and P4VP with PVPhMMA50, respectively.

In our previous study, we have obtained similar results concerning the blends of poly(styrene-*co*-4-vinyl pyridine) (PS4VP) copolymers with poly(styrene-*co*-methacrylic acid) (PSMA20) containing 20 mol % of methacrylic acid (MA).¹⁹ This trend could be due to the presence of strong specific interactions between PS4VPy and PVPhMMA50 copolymers, where these blends are able to form interpolymer

complexes. Indeed, it is important to note that the higher T_g s are obtained, for each system, when particularly the composition of PS4VP4 is in excess. As can be seen in Figure 2, the maximum of specific interactions may be found approximately at a ratio 1/3 of systems PVPhMMA50/ PS4VPy.

The influence of copolymer composition of PS4VP on the miscibility behavior is also examined. For this reason, PVPhMMA50 is mixed with different PS4VPy copolymers in a weight ratio 1/1. The variation of obtained glass transition (T_g s) with copolymer composition in 4VP wt % reveals two phase behavior type that can be expected according to T_g values as displayed in Figure 3. Less than 20 wt % 4VP in PS4VPy, the blends exhibit two T_g s corresponding approximately to their pure constituents. When the copolymer composition is rather between 20 and 30 wt %, two T_g s intermediate to those of PVPhMMA30 and PS4VPy are observed reflecting their partial miscibility. However, the mixtures containing copolymer with 30 wt % or plus of 4VP are characterized by a single T_g indicating their miscibility.

In order to analyze the miscibility of polymer blends, many approaches have been developed to describe the variation of T_g -composition in blends. One of the most widely used equation to describe the variation of T_g with composition is that described by Gordon-Taylor developed initially for miscible blends when this miscibility is not due to strong specific interactions. To account for the specific interactions that may be occurring between the unlike species in blends PS4VPy/PVPhMMA, we applied the Kwei expression, arising from the Gordon-Taylor, which seems to be adequate to predict the variation of T_g -composition particularly when the specific interactions are strong²⁰:

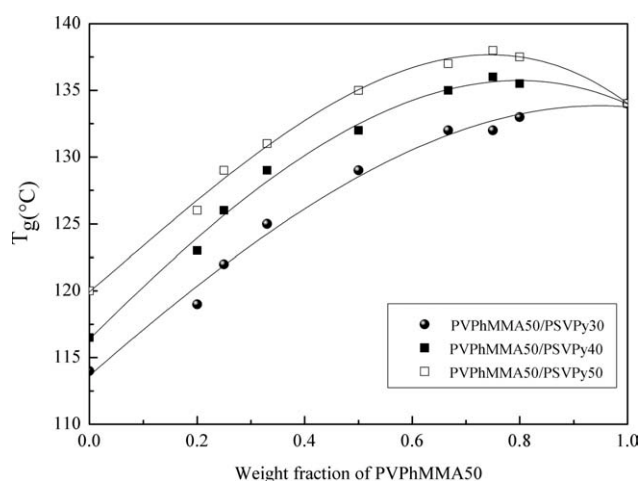


Figure 2 T_g -composition variation versus PVPhMMA50 weight fraction of PVPhMMA50/PS4VPy systems.

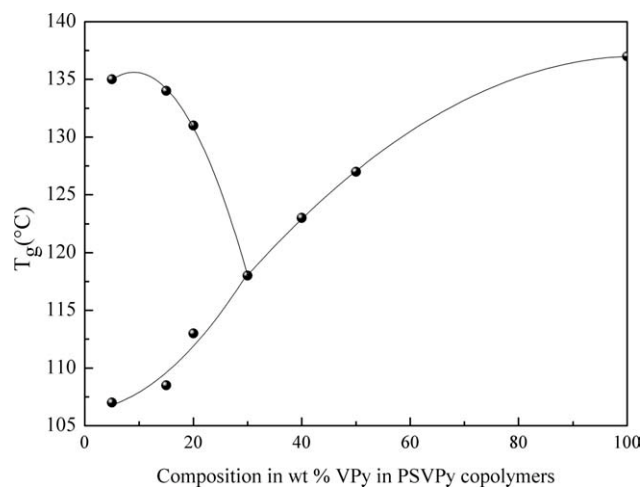


Figure 3 T_g -composition variation versus percentage of 4VPy of PVPhMMA50/PS4VPy systems in ratio 1 : 1.

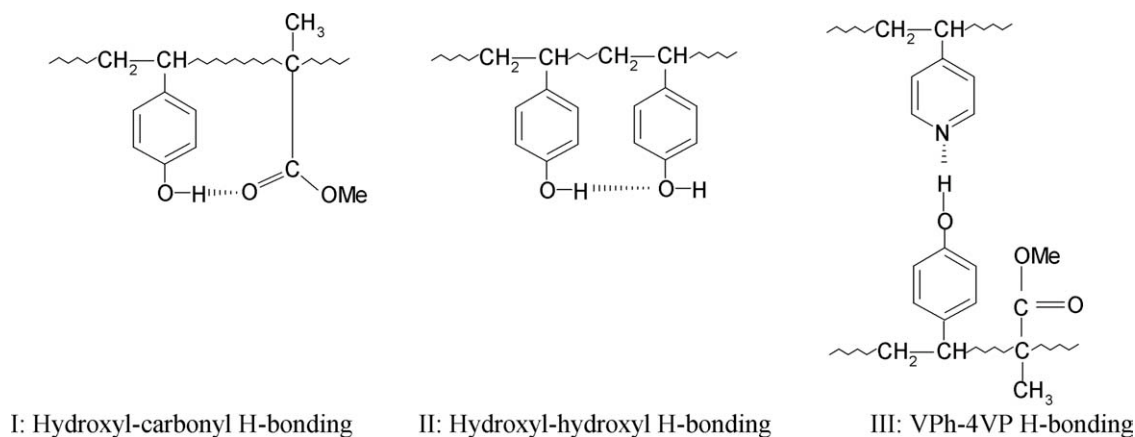
$$T_{g,\text{blend}} = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + q w_1 w_2 \quad (1)$$

where $T_{g,\text{blend}}$, is the glass transition temperature on the blend, w_1 and w_2 and T_{g1} and T_{g2} are the weight fractions and glass transition temperatures, respectively, of the corresponding constituents. The k and q are adjustable parameters related to the degree of curvature of the T_g -composition plots. The q constant measures the strength of the specific interactions that occurred between the two copolymers.

It is important to note that the q values obtained by curve fitting of traces T_g -composition increases progressively with increasing of VPy content in PS4VPy copolymers, indicating that the chain mobility is more restricted. This phenomenon could be related to the formation of intermolecular interactions between hydroxyl groups of VPh and nitrogen atom of vinylpyridine (VPy). Thus, the introduction of the basic sites may act as precursor to remove certain intramolecular hydrogen bonding that occurred between hydroxyl-hydroxyl and hydroxyl-carbonyl groups in PVPhMMA 50. This evolution confirms the presence of the stronger hydrogen-bonding interaction with increasing the amount of 4-vinylpyridine in both blends between unlike species. The Scheme 1 illustrated the potential specific interactions that can be involved in this system, where three different potential hydrogen-bonding interactions such as hydroxyl-hydroxyl, hydroxyl-carbonyl, and hydroxyl-pyridine are susceptible to form.

FTIR Study

It is well known that the presence of different chemical groups in the polymer blends often leads to several types of repulsive and/or attractive interactions. For this reason, FTIR spectroscopy is mostly used to



Scheme 1 Potential interactions involved on PVPhMMA50/PS4VPy systems in the carbonyl stretching region.

explore this type of interactions. It is proven to be a powerful technique to study the specific interactions.²¹ It is particularly suitable for the detection of specific interactions when the hydrogen bondings are present. However, it has been suggested that the hydrogen-bonding interactions considerably affect the energy of the covalent bonds on interactive species; hence, a frequency shift can be detected. The IR carbonyl-hydroxyl stretching range or flexion mode of pyridine-hydroxyl interactions is mainly sensitive to the hydrogen-bonding formation.

The first step will be devoted to putting in evidence these interactions such as hydrogen bonding present in the various binary mixtures PS4VP/PVPhMMA using infrared spectroscopy FTIR. The second step will be devoted to quantifying these interactions using the deconvolution methods will then be carried out in appropriate areas such as in carbonyls stretching frequency 1780–1650 cm^{-1} and in pyridine flexion mode 1650–1550 cm^{-1} , respectively. In this context, our interest here is focused to explore this type of specific interactions into miscible blends such as PSVP30/PVPhMMA50 by FTIR. It is important to note that the general features of the obtained infrared spectra of pure PS4VPy30 and PVPhMMA50, recorded in the range 400–4000 cm^{-1} , are entirely reliable with those expected for the respective copolymers and in good agreement with those obtained in the literature.^{22–24}

Figure 4 displays partial FTIR spectra in 1570–1640 cm^{-1} region recorded at 25°C for various PS4VPy30/PVPhMMA50 compositions. In this domain, the infrared spectrum of pure PVPhMMA50 copolymer exhibits two characteristic bands at 1595 and 1613 cm^{-1} . The first is assigned to phenyl rings modes, whereas the second band appeared at 1613 cm^{-1} is particularly important and lead us to believe that it may be ascribed to phenol rings when specific interactions such as hydrogen bonded of various strengths are favorable to form between

hydroxyl-hydroxyl and/or hydroxyl-carbonyl groups. It must be noted that this later band shift progressively toward lower wavenumbers that which is indicative that probably some of these interactions have been broken.

The infrared spectrum of pure PS4VPy30 copolymer is characterized by one broad band between 1601 and 1597 cm^{-1} assigned to styrene and pyridine rings. As can be seen, when the composition of PS4VPy30 increases in blend, three points may be mentioned. The latter band (1601 cm^{-1}) observed with the pure PS4VPy30 shifts slightly to higher wavenumbers and becomes more intense with increasing PS4VPy content in the blend. Therefore, the band detected at 1613 cm^{-1} in pure PVPhMMA50 shifts toward lower frequencies with the addition of PS4VPy30. A new band appears at 1607 cm^{-1} . A spectral shift of this magnitude may reasonably be taken as evidence of a specific interaction that occurs between the hydroxyl group and the nitrogen atom of VPy.

These changes reveal, in fact, that a new contribution corresponding to associated pyridine rings when the hydrogen bonds are formed between hydroxyl groups of PVPhMMA and nitrogen atom

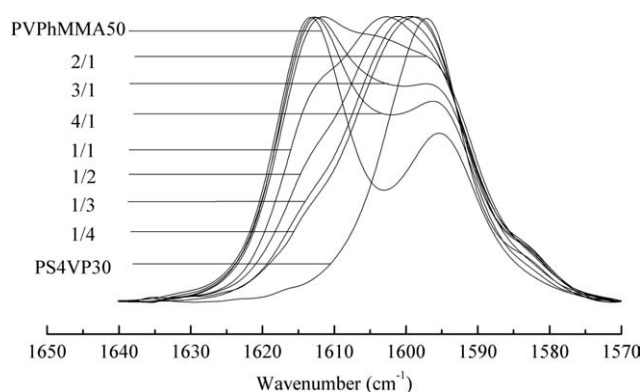


Figure 4 FTIR spectra of PVPhMMA50, PS4VPy30, and their blends in 1570–1640 cm^{-1} region.

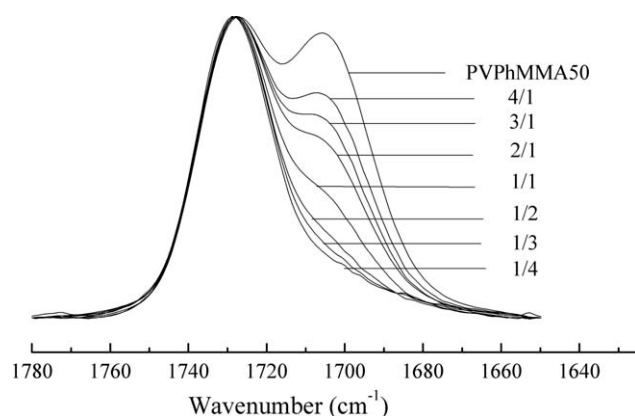


Figure 5 FTIR spectra of PVPhMMA50, PS4VPy30, and their blends in 1650–1780 cm^{-1} region.

of pyridine in PS4VPy30. It must be noted that the similar phenomena have been observed very recently in blends of PS4VPy and poly(styrene-*co*-methacrylic acid) which this band was attributed to associated pyridine.²⁵ Moreover, we have not observed the formation of any pyridinium ion for all systems. The shift toward lower frequency which can be ascribed as an increase in the rigidity of the pyridine rings and may be also considered as an evidence of the presence of the hydrogen bonding between PS4VPy30 and PVPhMMA50.

On the other hand, the carbonyl stretching (1650–1750 cm^{-1}) region is particularly important for two reasons. First, the PS4VPy copolymers show no absorptivity in carbonyl region starting from 1650 to 1760 cm^{-1} , whereas the pure PVPhMMA50 shows two characteristic bands observed at 1728 and 1705 cm^{-1} . These bands are respectively attributed to free carbonyl stretching vibrations (not hydrogen bonded) and to those that are self-associated (hydrogen bonded) with hydroxyl groups of VPh. This latter is more extensive than of the free one. However, the carbonyl stretching may certainly be affected by the presence of eventual hydrogen-bonding interactions. As an example, Figure 5 shows a scale-expanded FTIR spectrum in the carbonyl

region of PS4VPy30, PVPhMMA50, and their blends in different ratios. In addition, it can be clearly seen that the relative absorbance of the hydrogen bonded of carbonyl stretching band observed at 1705 cm^{-1} of pure PVPhMMA50 decreases progressively with increasing of PS4VPy30 composition in blend and shifted slightly to a higher frequency. This is may be due to the breaking of certain self-association between hydroxyl groups of PVPh and carbonyl groups of MMA groups.

The obtained results were corroborated with those that we have concluded very recently and, of course, in good agreement with those obtained previously by Coleman et al.²¹ Similar observations have been also made by Chang and coworkers in their study of blends of poly(vinylphenol-*co*-methyl methacrylate) with poly(ethylene oxide).^{26,27} We note that the similar behavior is also observed in other P4VPPhMMA50/PS4VPy systems.

The pyridine flexion mode observed at 1597 cm^{-1} is mainly perturbed when the hydrogen bonded interaction is developed. When PS4VPy30 added in blend, the new band appears at higher frequencies (up to 1607 cm^{-1}) clearly identified, which could be attributed to associated pyridine. Unfortunately, the band observed at 1597 cm^{-1} is rather difficult to analyze due to its overlap with the 1601 cm^{-1} band of phenyl rings of styrene and VPh segments. Although a quantitative analysis is relatively complex in this region, we have attempted to determine the fraction of free and associated pyridine using adequate curve fitting by the following equation³:

$$f_{\text{free}}^{\text{Pyr}} = \frac{A_{\text{free}}^{\text{Pyr}}}{A_{\text{free}}^{\text{Pyr}} + \left(\frac{a_{\text{Ass}}}{a_{\text{free}}}\right)A_{\text{Ass}}^{\text{Pyr}}} \quad (2)$$

where $A_{\text{free}}^{\text{Pyr}}$ and $A_{\text{Ass}}^{\text{Pyr}}$ are the peak areas corresponding to absorptions from free and associated pyridine, respectively. The absorptivity coefficient (a) is the specific absorption ratio of these bands ($a = a_{\text{Ass}}/a_{\text{free}}$). In our case, we assume that they have the same absorption coefficient, that is, a equals to unity.

TABLE II
Curve Fitting Data from Infrared Spectra of PVPhMMA50/PS4VPy30 Blends in the 1550–1650 cm^{-1} Region

PVPhMMA50/PS4VP30	Free pyridine			Associated pyridine		
	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	f_{free} (Pyr)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	f_{Ass} (Pyr)
80/20	1597	11	0.37	1606.1	8.00	0.63
75/25	1596.9	10.8	0.38	1607.0	7.62	0.62
67/33	1596.7	10.11	0.42	1606.9	7.40	0.58
50/50	1597.2	10.7	0.54	1607.0	7.21	0.46
33/67	1596.8	10.4	0.62	1605.9	6.90	0.38
25/75	1596.1	9.8	0.72	1606.4	6.73	0.28
20/80	1595.6	9.6	0.803	1605.5	7.00	0.197

$W_{1/2}$: Width at the half-height.

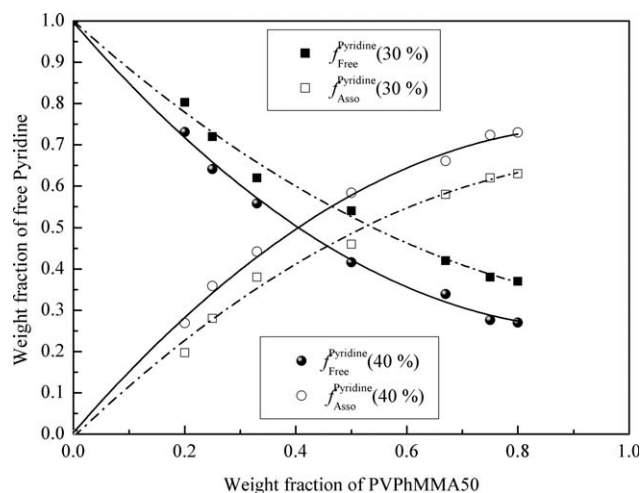


Figure 6 Evolution of associated pyridine and carbonyl fractions versus PS4VPy30 composition in blends.

Using an appropriate curve fitting method, the fractions of free and associated pyridine of PS4VPy30/PVPhMMA are calculated and summarized in Table II. It can be shown that the hydrogen-bonded fraction of the associated pyridine ring increases with the amount of PVPhMMA50 in the blend, whereas the free pyridine fraction decreases. In other words, this is indicative of the presence of specific interactions. For example, Figure 6 shows the evolution of free and associated pyridine of PVPhMMA50/PS4VP30 and PVPhMMA50/PS4VP40 blends. As can clearly be seen, the associated pyridine fraction is very important in the PVPhMMA50/PS4VP40 than those obtained in PVPhMMA50/PS4VP30. This indicates the ability of basic sites of VP segments to interact with the hydroxyl groups. Therefore, we believe that these results may be due to the preferential intermolecular interactions between unlike species comparatively to self-associated hydroxyl–hydroxyl and/or hydroxyl–carbonyl groups.

Additionally, the free and associated carbonyl fractions were also calculated by the following equation using an adequate curve fitting:

$$f_{\text{free}}^{\text{C=O}} = \frac{A_{\text{free}}^{\text{C=O}}}{A_{\text{free}}^{\text{C=O}} + aA_{\text{Asso}}^{\text{C=O}}} \quad (3)$$

where A is the peak areas corresponding to free, associated carbonyls. The absorptivity ratio (a) is assumed equal to 1.5.³ Table III summarized the free and associated carbonyl fractions for PVPhMMA50/PS4VPy30 system. The careful examination of the obtained values of these fractions may be taken to indicate that the hydrogen bonded carbonyl fraction decreases intimately with increasing 4VPy content in the blend, while that of free carbonyls remains fairly constant. This is in good agreement with those obtained previously by Coleman et al.²¹ On the other hand, we suggest that the hydrogen bond interactions occurring between the hydroxyl groups of PVPh and the nitrogen atom of 4VPy are formed by breaking the strong inter and/or intramolecular hydrogen bonds present at the pure PVPhMMA50.

SEM Study

The morphology of the two systems PVPhMMA50/PS4VPy05 in ratios (75/25, 50/50, and 25/75) and PVPhMMA50/PS4VPy30 (50/50) was examined by scanning electron microscopy. In agreement with the DSC and FTIR results presented above, the scanning electron micrographs of the fractured surfaces shown in Figure 7 confirm, unambiguously, the heterogeneity of these blends when the composition of vinylpyridine (4VPy) in PS4VPy copolymers is less than about 20%. This could be interpreted as to their immiscibility. However, The progressive addition of the amount of 4VP (from 30%) in PS4VP copolymers leads to finer and more regular dispersion of phase, which means to form homogenous structure necessary to ensure good mechanical properties of the blends. An improved PS4VPy30 dissolution in PVPhMMA50 phase is however observed when this one is in excess.

TABLE III
Curve Fitting Data from Infrared Spectra of PVPhMMA50/PS4VPy30 Blends in the 1670–1680 cm^{-1} Region

Blend composition	Free C=O			Hydrogen bonded C=O		
	Frequency	Width	Fraction	Frequency	Width	Fraction
PVPhMMA50/PS4VP30	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	f_{free}	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	f_{Asso}
82/20	1728	22	0.081	1705	28	0.615
75/25	1727	22	0.061	1704	27	0.600
67/33	1728	21	0.064	1705	28	0.572
50/50	1728	22	0.032	1704	29	0.545
33/67	1729	20	0.013	1705	28	0.457
25/75	1728	22	0.023	1706	29	0.402
20/80	1728	22	0.023	1705	28	0.402

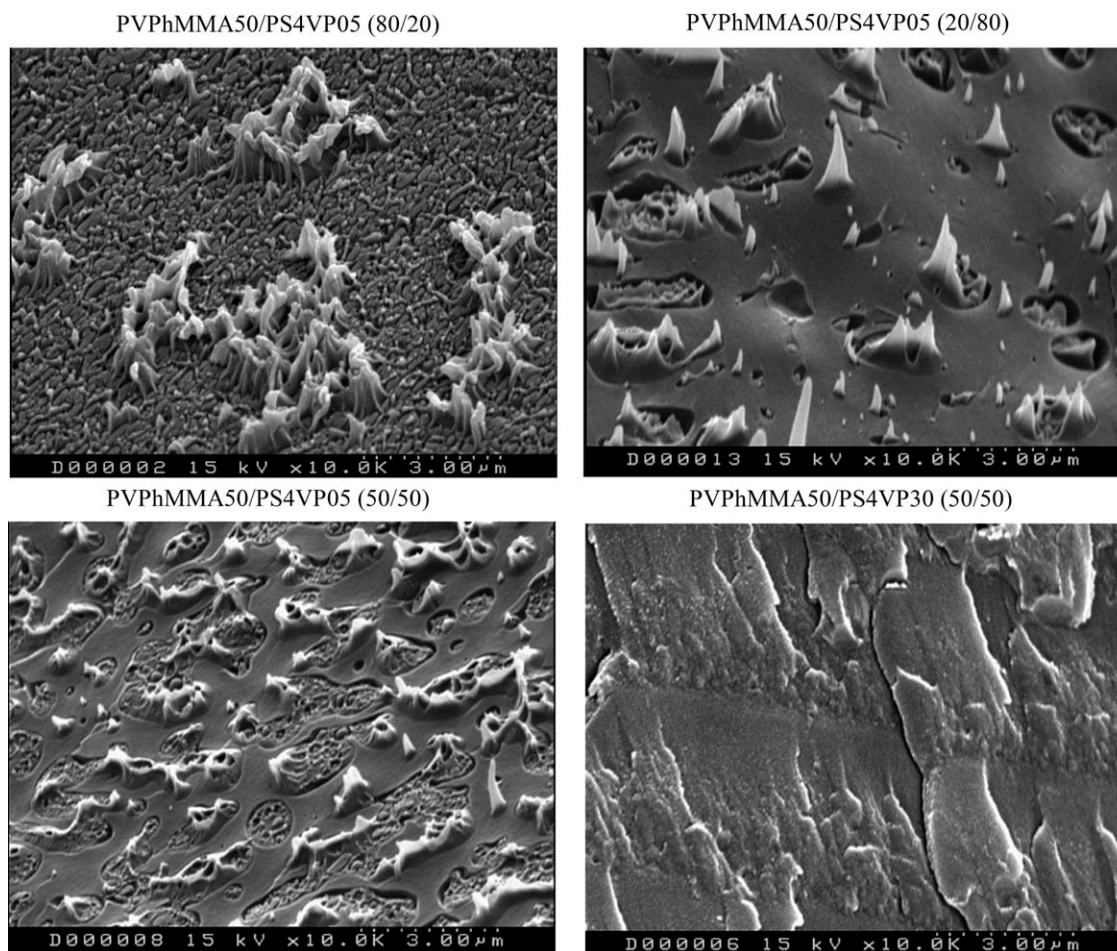


Figure 7 SEM photomicrographs of PVPhMMA50/PS4VPy05 blends in three different ratios (75/25, 50/50, 25/75) and PVPhMMA50/PS4VPy30 in ratio 50/50.

CONCLUSIONS

The miscibility and phase behavior of PVPhMMA50 with a variety of PS4VP copolymers have been investigated by DSC, FTIR, and SEM. The obtained results show that depending on the densities of basic groups introduced within PS, two phase behavior types are observed. Less than 30 wt % VP content in PS4VP copolymers, heterogeneous phase behavior is observed and evidenced by the apparition of two T_g s. However, from 30 wt % of VP in blends, this miscibility or complexation was first evidenced by DSC where a single T_g was detected for each composition of the blends.

It has been shown that the blends of PVPhMMA50 with PS4VPy40, PS4VPy50, and P4VP had, for each composition, a single T_g higher than those obtained for the pure constituents, which may be taken to indicate that PVPhMMA50 interacts more strongly with PS4VPy when VPy wt % content increases. The T_g -composition trace of blends in a ratio of 50/50 indicates clearly that the obtained T_g s depend strongly on the amount of VPy in PS4VPy copolymers.

FTIR results revealed that the hydroxyl groups of phenol rings interact preferentially with the pyridyl groups through hydrogen-bonding interactions as evidenced by the decreasing of frequency intensities corresponding to self-association hydroxyl-carbonyl localized at 1705 cm^{-1} with increasing of VPy units in blends. The presence of the hydrogen-bonding interactions between hydroxyl groups and nitrogen atom of the VPy is also evidenced qualitatively by apparition of a new band at 1607 cm^{-1} attributed to associated pyridine and quantitatively from the evaluation of the fractions of free and associated carbonyl and pyridine groups in their corresponding regions.

As confirmed by SEM, a better dispersion of blends PSVPhMMA50/PS4VPy have been obtained when the composition of VPy in PS4VPy copolymers greater than 30 wt % may be considered as a result of strong intermolecular interactions that occurred between unlike species.

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