

Article

Miscibility and Hydrogen Bonding in Blends of Poly(4-vinylphenol)/Poly(vinyl methyl ketone)

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Abstract: The miscibility and phase behavior of poly(4-vinylphenol) (PVPh) with poly(vinyl methyl ketone) (PVMK) was investigated by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). It was shown that all blends of PVPh/PVMK are totally miscible. A DSC study showed the apparition of a single glass transition (T_g) over their entire composition range. When the amount of PVPh exceeds 50% in blends, the obtained T_g s are found to be significantly higher than those observed for each individual component of the mixture, indicating that these blends are capable of forming interpolymer complexes. FTIR analysis revealed the existence of preferential specific interactions via hydrogen bonding between the hydroxyl and carbonyl groups, which intensified when the amount of PVPh was increased in blends. Furthermore, the quantitative FTIR study carried out for PVPh/PVMK blends was also performed for the vinylphenol (VPh) and vinyl methyl ketone (VMK) functional groups. These results were also established by scanning electron microscopy study (SEM).

Keywords: differential scanning calorimetry (DSC); fourier transform infrared spectroscopy (FTIR); miscibility; hydrogen bonding; polymer-blend

1. Introduction

The elaboration of new polymer materials with improved properties has been the subject of much academic and industrial research. Several theories and methodologies have been regularly proposed in order to improve their properties. In fact, the homogeneity of polymer materials is often considered as being a key factor in the substantial improvement of some properties, such as processability, impact strength, tensile strength, chemical resistance, *etc.* Unfortunately, it has been established that in most cases, the polymer blends are incompatible, due to their high molecular weight and weak or unfavorable interactions between unlike species in a binary mixture [1–3]. This behavior is, generally, undesirable, because the materials obtained from immiscible blends often possess poor thermal and mechanical properties, which consequently restricts their use in a wide range of industrial applications.

In this context, polymer blending has been proven to be an effective alternative in obtaining new materials with improved properties, such as better processability and low cost, among others. Thus, as the contribution of the mixing entropy of polymer blends is generally negligible ($\Delta S_{\text{mix}} \sim 0$), the miscibility of polymer blends is mainly dependent on the value of mixing enthalpy (ΔH_{mix}). For this purpose, to obtain a miscible blend system, it is usually necessary to guarantee that the enthalpy of mixing should be negative, reflecting the presence of favorable specific interactions between the components or sufficient intramolecular repulsions between unlike species of the blends [4–7].

Many methods have been developed to study the miscibility of binary or ternary polymer blends. Among them, the introduction of specific interactions, within two unlike constituents, by copolymerization seems to be a frequently used effective method. It has been reported that two homopolymers, which initially form an immiscible system, could enhance their compatibility by introducing the complementary chemical structures capable of establishing specific interactions between their chains. Panayiotou *et al.* studied blends of poly(styrene-*co*-vinylphenol) (PSVPh) with polyvinylpyrrolidone (PVP) and found that the copolymers of PSVPh containing more than 4 mol% vinyl phenol become totally miscible with polyvinylpyrrolidone over the whole blend range composition; while the copolymers, PSVPh, containing more than 25 mol% vinyl phenol, form complexes, which precipitate in solution with a common solvent [8]. Recently, we studied the phase behavior and miscibility of blends of poly(vinylphenol-*co*-methyl methacrylate) (PVPhMMA50) containing 50 mol% of methyl methacrylate with copolymers of poly(styrene-*co*-4-vinylpyridine) (PS4VPy). We demonstrated that, depending on the densities of basic groups introduced within polystyrene, two phase-behavior type is observed. In blends with less than 30 mol% VP content in PS4VP copolymers, a heterogeneous phase is observed and evidenced by the apparition of two T_g s. However, in the copolymers, PS4VPy, containing more than 30 mol% of vinyl pyridine in PS4VPy, this miscibility or complexation is also evidenced by differential scanning calorimetry (DSC), where a single T_g was detected for each composition of the blends [9].

Poly(vinylphenol) (PVPh) has been one of the most widely studied thermoplastics [10–13]. Structurally, it is similar to polystyrene with the junction of hydroxyl group in the para position of phenyl. It has been found very suitable for tissue engineering and in electronics as a dielectric layer in organic transistors and in organic thin-film-transistor liquid-crystal displays (TFT LCD). In addition, poly(vinyl methyl ketone) (PVMK) is an interesting synthetic polymer with a broad range of industrial applications. It has become of greater interest because of improved processes for its preparation.

PVMK is widely used in cross-linked thin films. It can be also used in some electronic applications, often in combination with pentacene [14]. The presence of carbonyl groups in the structure of PVMK is particularly interesting in order to develop specific interactions, such as the hydrogen bond type with hydroxyl groups of PVPh.

In this contribution, the phase behavior and miscibility of blends of poly(vinylphenol) (PVPh with poly(vinyl methyl ketone) (PVMK) will be explored. The miscibility of these binary blends will be studied by means of DSC, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). The phase behavior and miscibility of these blends according to their glass transition temperatures (T_g s) was examined by means of DSC. Moreover, the possible specific interactions, such as hydrogen bonding, will be studied qualitatively and quantitatively by FTIR.

2. Experimental Section

Poly(4-vinylphenol) (PVPh) and poly(methyl ketone) (PVMK) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received.

Blends of poly(4-vinylphenol) and poly(methyl ketone) 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 (Waltham, MA, USA) equipped with an intracooler. All T_g measurements were carried out at a heating rate of 20 °C/min under nitrogen flow. Each T_g was obtained from the second scan, and its value was taken as the midpoint of the transition of the second scan.

FTIR measurement was recorded on a Nicolet Magna 560 FTIR spectrometer (ThermoFisher, Waltham, MA, USA), and 32 scans were collected with a spectral resolution of 2 cm^{-1} . The 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 of the samples were dried to a constant weight in a vacuum oven at 60 °C for several days to evaporate the solvent slowly. The different samples of PVPh/PVMK blends were fractured cryogenically, and their scanning electron micrograms were taken with a HITACHI S2700 scanning electron microscopy (Chiyoda, Tokyo, Japan). The characteristics of these polymers are given in Table 1.

Table 1. Polymer characteristics.

Polymers	M_w	M_w/M_n	T_g (°C)
PVPh	150,000	1.74	158
PVMK	500,000	–	37.5

3. Results and Discussion

3.1. DSC Study

Qualitative tests of the miscibility of these blends using THF as the solvent were carried out. For all blend compositions, a single phase formation suggesting their homogeneity was observed. In addition, the formation of a small amount of complex in solution was also detected in the blends containing an

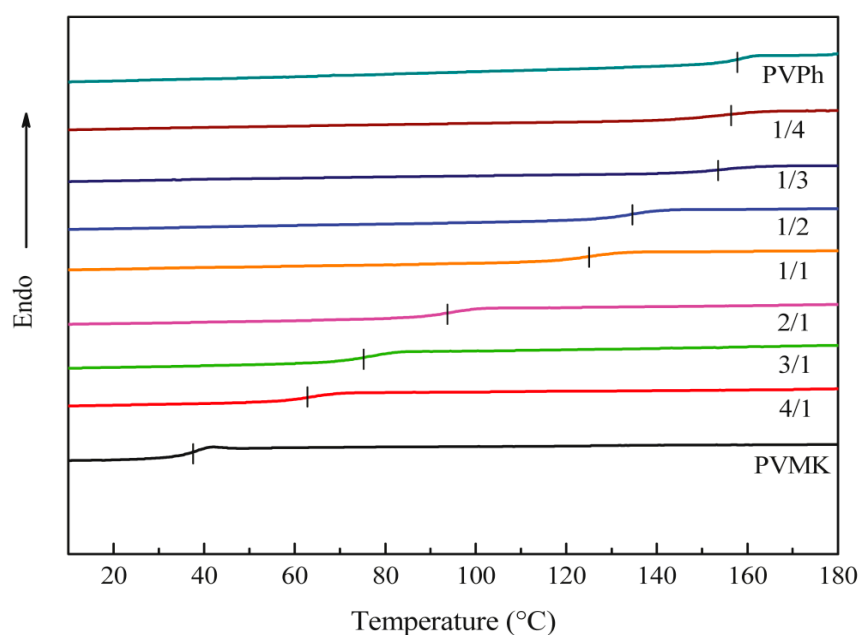
excess of polyvinyl phenol. This reveals the formation of the interconnection interactions between the unlike species.

Many techniques have been used to investigate the phase behavior and miscibility of polymer blends. Owing to their simplicity and speed, thermal analysis and spectroscopic techniques are the ones most commonly used. These techniques offer information about the miscibility in the different range scales. Hence, the observation of a single glass transition for polymer blends determined by DSC clearly shows the compatibility of the blend on a scale of 20–30 nm. Moreover, the transition behaviors observed with the polymers have long been used as a basic criterion in the study of the miscibility of polymer blends. Therefore, 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 occurring at the segments level during the transition [15].

For this purpose, the DSC is the most useful method for elucidating the miscibility of polymer blends. It has been able to provide good and reliable information about the morphology and the possible orientations that could be taking place between different chains. Furthermore, it has been established that the observation of a single glass temperature transition (T_g) among the pure constituents is indicative of their miscibility; while the detection of the two T_g s corresponding to the initial components, respectively, indicates their immiscibility [16–18].

The thermograms corresponding to PVPh, PVMK and their blends of different compositions are displayed in Figure 1. One glass transition temperature is observed with each composition between those of the pure constituents, PVPh and PVMK, respectively.

Figure 1. DSC thermograms of poly(4-vinylphenol) (PVPh)/poly(vinyl methyl ketone) (PVMK) blends.



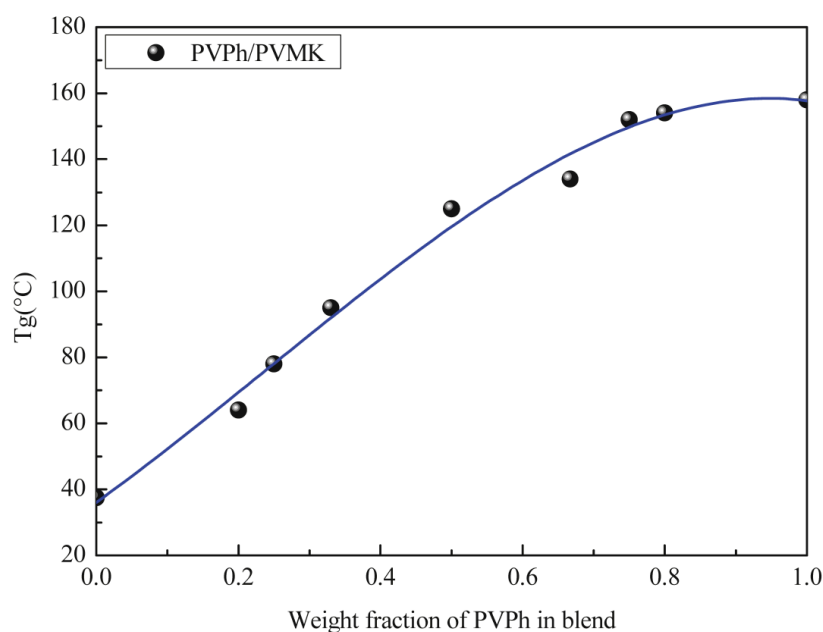
The variation of the obtained T_g s with the composition of polyvinyl phenol in the mixture is illustrated in Figure 2. The observation of the single glass transition temperature (T_g) for each composition may be evidenced as indicative of their miscibility. Moreover, it can be seen that the

T_g -composition curve deviated positively from the weight average of the pure components T_g s. In our previous study, we observed similar behavior with the blends of poly(vinylphenol-*co*-methyl methacrylate) and poly(styrene-*co*-vinylpyridine) [14]. This trend is commonly attributed to the presence of a strong specific interaction that occurred between unlike species. For all compositions, the values of T_g , reveal clearly that these blends are able to form interpolymer complexes and confirm which was observed during the preparation of solutions. In addition, the intensity of these interactions with the content of the interacting species in the polymeric chains was qualitatively estimated from the T_g -composition curve displayed in Figure 2 and described by the Kwei equation [9]:

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

where w_1 , w_2 , T_{g1} and T_{g2} are the weight fractions and glass transition temperatures of the corresponding constituents. The q constant relates the extent of the specific interactions that occurred between the components in the blends.

Figure 2. T_g -composition variation *versus* PVPh weight fraction of the PVPh/PVMK system.



It is important to note that the obtained values of q (~88) for blends of PVPh/PVMK are relatively higher than those obtained previously for the blends of PVPhMMA50/PVMK. It seems that this result is predictable; in fact, a fraction of hydroxyl groups of vinylphenol in PVPhMMA50 is involved in intra-molecular interactions with carbonyl groups of methyl methacrylate (MMA). On the other hand, these interactions compete with the self-association of hydroxyl groups that are not present in the blends of PVPh/PVMK.

3.2. 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 explore these types of interactions [19]. It is particularly suitable for the detection of specific

interactions when the hydrogen bonding is present. However, it has been suggested that the hydrogen bonding interactions can occur in any system containing a proton donor group and a proton acceptor. The strength of the bond considerably affects the energy of the covalent bonds on interactive species; hence, a frequency shift can be observed. In fact, the stretching frequency of the acceptor group, such as the carbonyl group C=O, is also moved to lower frequencies (longer wavelengths), usually with an increased intensity of hydrogen bonding.

On the other hand, the hydroxyl group of the phenol ring (H–O) bending vibration usually shifts to a shorter wavelength when bonding occurs; this shift is less pronounced than that of the stretching frequency. The IR carbonyl-hydroxyl stretching range or flexion mode hydroxyl-hydroxyl interactions are also sensitive to the hydrogen bonding formation.

Firstly, we explored interactions, such as hydrogen bonding present in the binary mixtures PVPh/PVMK qualitatively using infra-red spectroscopy FTIR. The second step was devoted to quantifying these interactions using deconvolution methods in appropriate areas, such as in the carbonyls' stretching frequency $1780\text{--}1650\text{ cm}^{-1}$. Scheme 1 shows the potential specific interactions that can be involved in this system, where two types of hydrogen bonding interactions, such as hydroxyl–hydroxyl, hydroxyl–carbonyl, can be formed.

Scheme 1. Potential hydrogen-bonding involved in the PVPh/PVMK system.

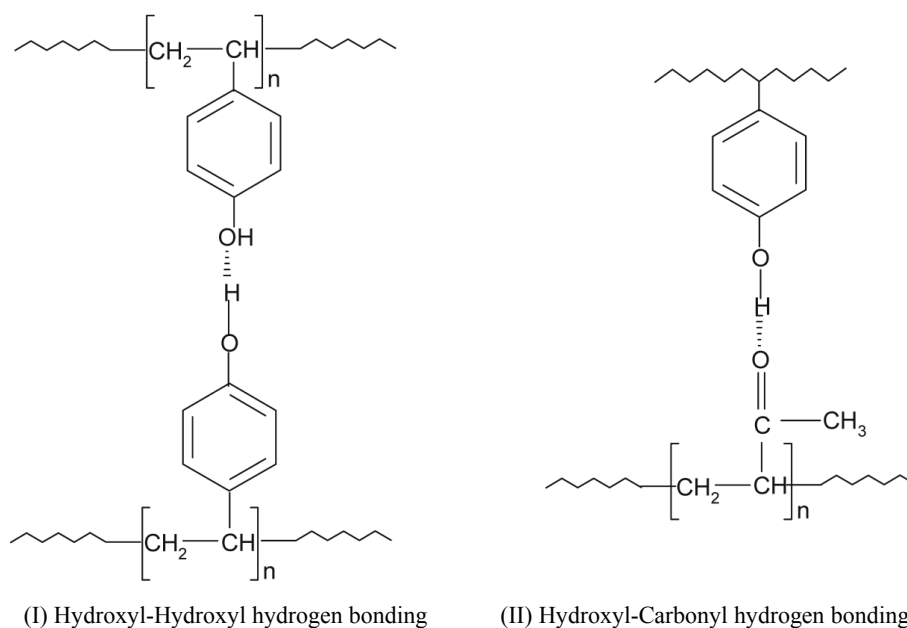
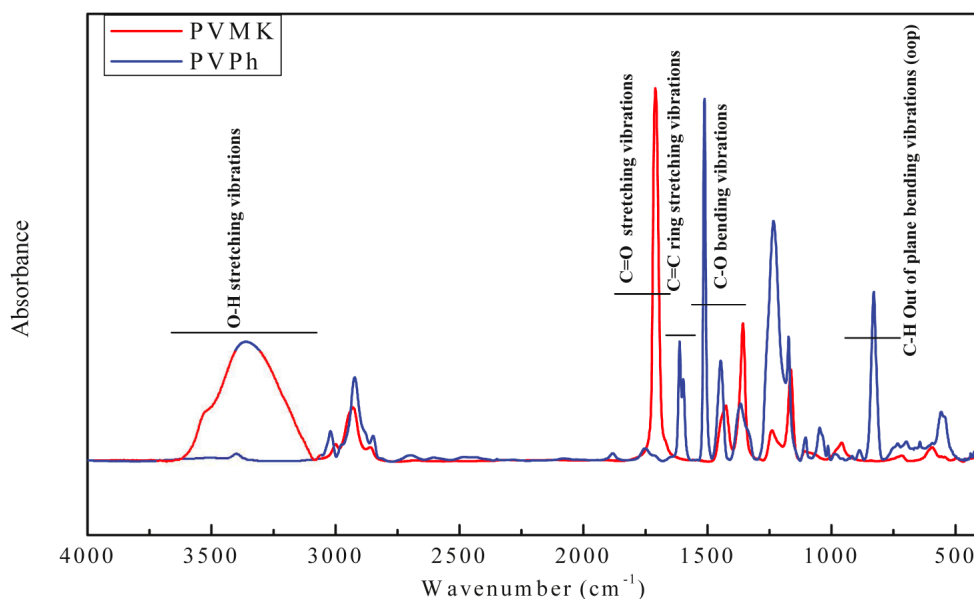
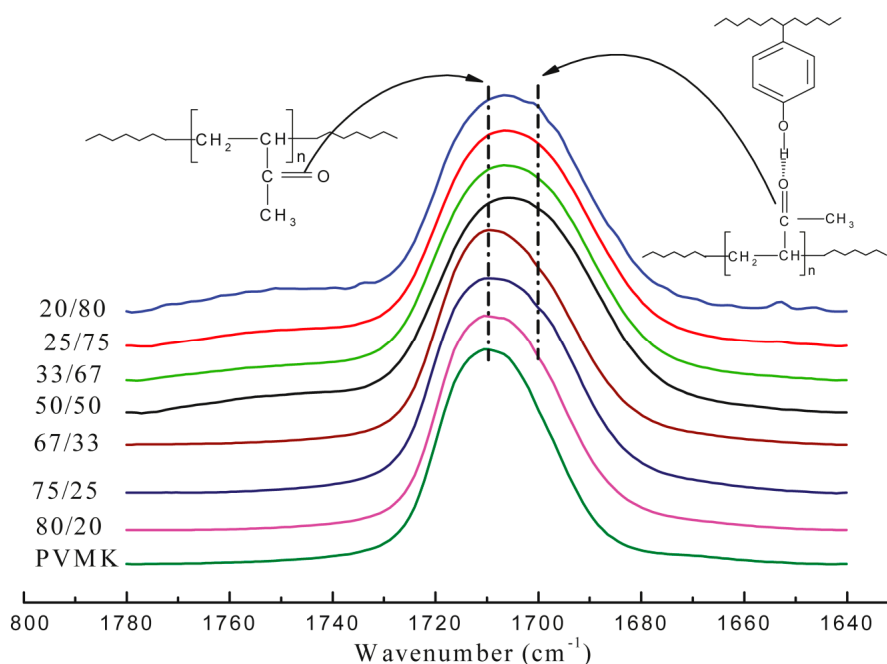


Figure 3 presents the FTIR spectra of two polymers used in this study. As can be seen in this figure, the carbonyl and hydroxyl regions are particularly important. For example, the first polymer (PVMK) is absorbed in the carbonyl region and does not give any band in the bending region of the hydroxyl groups. However, PVPh does not absorb in the first region, whereas it has two characteristic bands in the second one assigned, respectively, to free and associated hydroxyl groups of PVPh. It is important to note that the general features of the obtained infrared spectra of pure PVPh and PVMK, recorded in the range $400\text{--}4000\text{ cm}^{-1}$, are entirely consistent with those expected for the respective polymers and in good agreement with those obtained in the literature [20–22].

Figure 3. Infrared spectra of PVPh and PVMK in the 400–4000 cm^{-1} region.

As can be seen in the carbonyl stretching region (1650–1780 cm^{-1}), displayed in Figure 4, PVMK shows only one band localized at 1709 cm^{-1} assigned to free (non-hydrogen-bonded) carbonyl groups. When PVPh is added progressively, the carbonyl stretching band observed of pure PVMK shifted slightly to a lower frequency, due to the formation of hydrogen bonding between carboxylic and carbonyl groups of two polymers. The appearance of a new band is clearly identified at 1705 cm^{-1} , which is assigned to associated carbonyl as a consequence of the hydrogen bonding formed between unlike species.

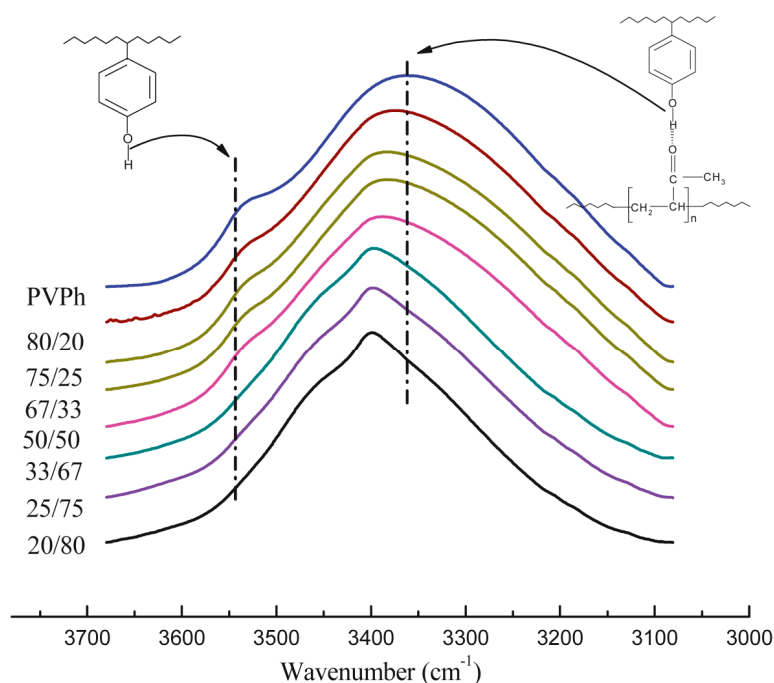
Figure 4. FTIR spectra of PVPh, PVMK and their blends in the 1650–1780 cm^{-1} region.

The hydroxyl stretching (3200–3550 cm^{-1}) region is particularly important for two reasons. First, the poly(vinyl methyl ketone) shows no absorption in this region starting, whereas the pure PVPh

shows two characteristic bands observed at 3522 and 3361 cm^{-1} . These bands are respectively attributed to free hydroxyl stretching vibrations (not hydrogen bonded) and to those that are self-associated (hydrogen bonded) with the hydroxyl groups (intra and/or inter) of PVPh. The latter is more intense than for the free one. However, the hydroxyl stretching may be affected by the presence of eventual hydrogen bonding interactions.

As an example, Figure 5 shows a scale-expanded FTIR spectra in the hydroxyl region of PVMK, PVPh and their blends in different ratios. Furthermore, it can be clearly seen that the relative absorbance of the associated hydroxyl-hydroxyl stretching observed initially at 3361 cm^{-1} of pure PVPh decreases progressively with the increase of the PVMK composition in the blend and shifts slightly to a higher frequency. This may be due to the formation of the hydrogen bonding that can occur between hydroxyl groups of PVPh and carbonyl groups of PVMK.

Figure 5. FTIR spectra of PVPh, PVMK and their blends in the 3050–3580 cm^{-1} region.



Due to the fact that the band observed at 1710 cm^{-1} , assigned to the free carbonyl of PVMK, is rather difficult to analyze, due to its overlap with the band that appears at 1705 cm^{-1} , attributed to an associated carbonyl, quantitative analysis is relatively complex in this region. In spite of this fact, we attempted to determine the fraction of free and associated carbonyl using adequate curve fitting by the following equation [23–25]:

$$f_{\text{free}}^{\text{C=O}} = \frac{A_{\text{free}}^{\text{C=O}}}{A_{\text{free}}^{\text{C=O}} + aA_{\text{Asso}}^{\text{C=O}}} \quad (2)$$

where A are the peak areas corresponding to free and associated carbonyls. The absorptivity ratio (a) is assumed equal to 1.5. 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, *i.e.*, it equals to unity. Table 2 summarizes the free and associated carbonyl fractions for PVPh/PVMK system choosing an appropriate curve fitting.

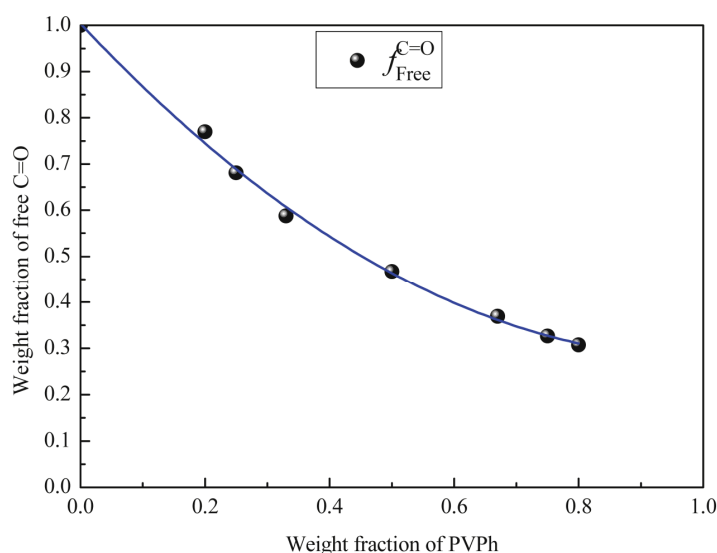
Table 2. Curve fitting data from infrared spectra of PVMK/PVPh blends in the 1650–1780 cm^{-1} region.

Blend Composition (PVMK/PVPh)	Free C=O			Hydrogen Bonded C=O		
	Frequency ν (cm^{-1})	Width $w_{1/2}$ (cm^{-1})	Fraction f_{free}	Frequency ν (cm^{-1})	Width $w_{1/2}$ (cm^{-1})	Fraction f_{Asso}
80/20	1710	20	0.770	1705	19	0.232
75/25	1710	21	0.681	1704	18	0.319
67/33	1710	21	0.588	1705	19	0.412
50/50	1709	21	0.467	1704	19	0.533
33/67	1710	20	0.369	1705	20	0.631
25/75	1710	22	0.326	1706	19	0.674
20/80	1709	21	0.307	1704	18	0.693

Data obtained by fixing the positions and widths at half-height (ν , $w_{1/2}$ cm^{-1}) of free carbonyl (1710 and 21, respectively) in the 1780–1650 cm^{-1} region.

The careful examination of the obtained values of these fractions may be taken to indicate that the free carbonyl fraction decreases intimately with increasing of PVPh content in the blend. This is in good agreement with those results obtained recently and with those suggested previously by Coleman and coworkers [3]. In addition, we suggest that the hydrogen bond interactions occurring between the hydroxyl groups of PVPh and the oxygen atom of PVMK are preferentially formed by breaking of the moderate inter- and/or intra-molecular hydrogen bonds present at the pure PVPh.

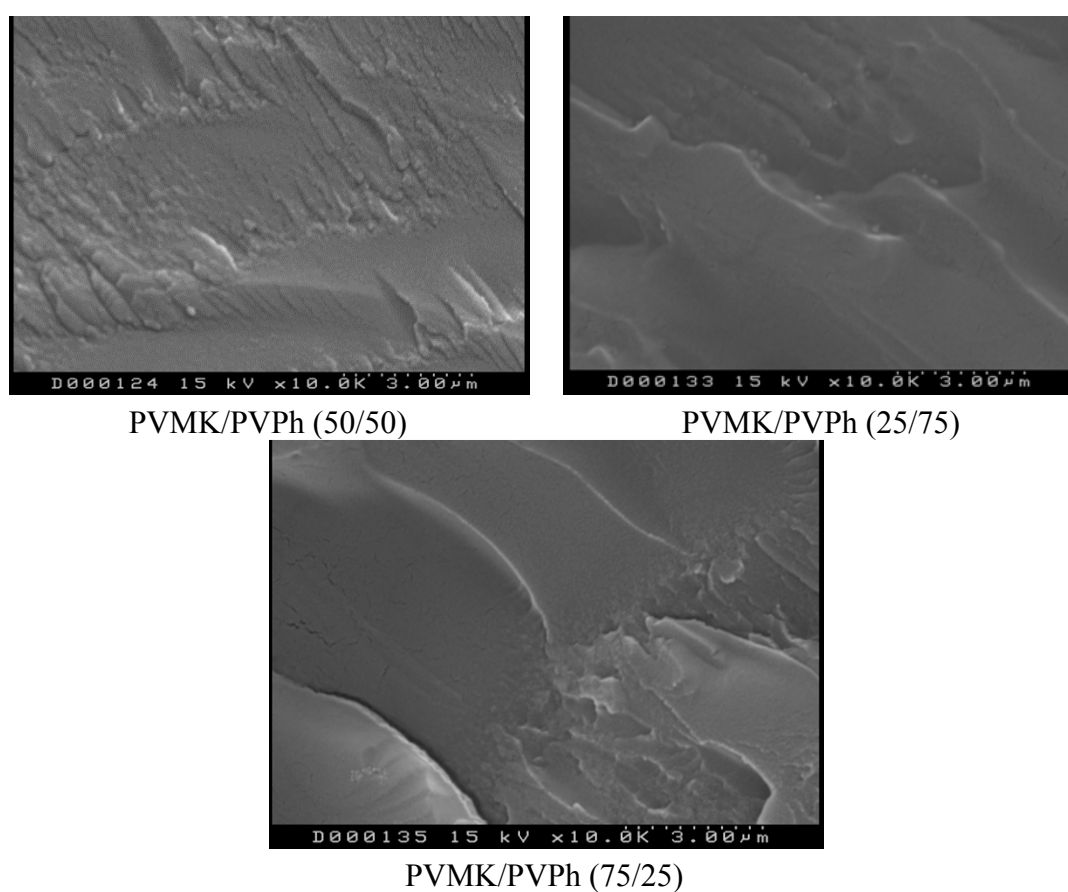
Figure 6 illustrates the evolution of free carbonyl fraction of PVMK as a function of PVPh composition in the blend. As can be seen in this figure, the free carbonyl fraction ($f^{\text{C=O}}$) of blends decreases progressively with increasing of the amount of PVPh in the mixture. On the other hand, we observe that the fraction of associated carbonyl increases by increasing the PVPh. This is indicative of the presence of specific interactions. Therefore, we believe that these results may be due to the preferential intermolecular interactions, which can occur between hydroxyl and carbonyl groups comparatively to self-associated hydroxyl-hydroxyl. Very recently, we obtained similar results concerning the blends of poly(vinylphenol-co-methyl methacrylate) (PVPhMMA50) with poly(vinyl methyl ketone) (PVMK) [26].

Figure 6. Evolution of free carbonyl fraction *versus* PVPh composition in blends.

3.3. SEM Study

The morphology of the two systems PVPh/PVMK in ratios (75/25, 50/50 and 25/75) 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 homogeneity of these blends in all ranges and can be seen as proof of their miscibility. However, the progressive addition of the amount of PVPh in blend leads to a finer and more regular dispersion of the phase, which suggests that a homogenous structure necessary to ensure the good mechanical properties of the blends is formed.

Figure 7. SEM photomicrographs of PVMK/PVPh blends in three different ratios (75/25, 50/50, 25/75).



4. Conclusions

The miscibility and phase behavior of PVPh with PVMK were investigated by DSC, FTIR and SEM. This miscibility was firstly evidenced by DSC, where a single T_g was detected for each composition of the blends. The positive deviation of T_g values from the additivity rule reveals that this miscibility may be due to the presence of specific interactions occurring between the two polymers.

FTIR results revealed that the hydroxyl groups of phenol rings interact preferentially with the carbonyl group through hydrogen bonding interactions, as evidenced by the decreasing of frequency intensities corresponding to free carbonyl localized at 1710 cm^{-1} by the increasing of PVPh in blends. The presence of the hydrogen bonding interactions between hydroxyl groups and the oxygen atom of

PVMK is also evidenced qualitatively by the apparition of a new band at 1705 cm^{-1} attributed to associated carbonyl. This trend is confirmed quantitatively from the evaluation of the fraction of free carbonyl of PVMK when PVPh is added in blends. As corroborated by SEM, a better dispersion of blends of PVPh/PVMK was also observed.

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Author Contributions

All measurements and characterizations were carried out by Hana Bourara, Slimane Hadjout and Agustin Etxeberria. Furthermore, they contributed to the writing of the paper. Zitouni Benabdelghani coordinated the study and the writing of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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