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Hydrogen Bonds in Blends of Poly(vinylphenol-*co*-methylmethacrylate)/Poly(vinylmethylketone)

Z. Benabdelghani,[*1] *A. Etxeberria*[2]

Summary: The hydrogen bonding and phase behaviour of blends of poly(vinylphenol-co-methylmethacrylate) (PVPhMMA50) containing 50% of methyl methacrylate with poly(vinylmethylketone) (PVMK) were investigated by differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). It was shown that all the blends have a single glass transition over the entire composition range. The FTIR study reveals the presence of intermolecular hydrogen-bonding interactions occurring between hydroxyl and carbonyl groups of vinylphenol (PVPh) and (PVMK) and intensified when the amount of PVMK increased in blend. A new band characterizing these interactions at 1713 cm^{-1} was observed. Furthermore, the quantitative FTIR study carried out for PVPhMMA50/PVMK blends was also performed for the vinylphenol and vinylmethylketone functional groups.

Keywords: blends; differential scanning calorimetry (DSC); FT-IR

Introduction

During the five decades, the polymer blending has been the focus of intense interest of a large scientific community from both academic and industrial points of view. It is an attractive approach to obtain new polymeric materials with large scale properties and a relatively low cost. 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 that can be occurring between the polymers.[1,2] It well known that the use of polymeric materials is often conditioned by their thermomechanical properties which are also depend on the mixing scale of these blends. It is therefore of great interest to investigate the miscibility and the phase behavior of polymer blends. Furthermore, 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 co-monomers of the blends.

In this context, several methods have been proposed. Among them, the introduction of specific interactions, within two dissimilar constituents by copolymerization has been widely used. Paul and coworkers have enumerated several cases of miscible binary blends involving copolymers when their corresponding homopolymers are not similarly miscible.[7] On the other hand, 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.[3–5]

Poly(vinylmethylketone)(PVMK) is interesting amorphous polymer. The carbonyl groups of this polymer have a strong capacity to form interactions with polar groups. Poly(vinylphenol-co-methylmethacrylate) (PVPhMMA50) is also an inter-

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[1] Faculty of Chemistry, University of Sciences and Technology (USTHB), P.O. Box 32, El Alia, Algiers 16111, Algeria
E-mail: ben_zit@yahoo.fr

[2] Departamento de Ciencia y Tecnología de Polímeros and Instituto de Materiales Polimericos (POLYMAT). Universidad del País Vasco UPV/EHU. P.O. Box 1072. 20080 San Sebastián, Spain

esting 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. Also, due to their high gas barrier proprieties, they are used in food packaging products. Furthermore, the hydroxyl groups of PVPhMMA50 are the only chemical groups available to develop strong interactions (hydrogen bond type) with carbonyl groups.

In this contribution, the phase behavior and miscibility of blends of poly(vinylphenol-co-methyl methacrylate) (PVPhMMA50) containing 50% in mol of methyl methacrylate with poly(vinylmethylketone) (PVMK) will be investigated. The miscibility of these binary blends is studied by means of DSC, FTIR and SEM. Firstly, we examined in detail by DSC the phase behavior and miscibility of these blends according to their glass transition temperatures (Tg's). Secondly, the possible specific interactions were studied qualitatively and quantitatively by Fourier transform infrared spectroscopy (FTIR). Moreover, the relationship between the observed phase behaviors of blends as determined by DSC, the formation of hydrogen bonding explored by FTIR.

Experimental Part

Polymers and Characterizations

Poly(4-vinylphenol-co-methyl methacrylate) (PVPhMMA50) containing 50 mol % of MMA and poly(vinylmethylketone) (PVMK) were purchased from Aldrich and used as received. Blends of poly(vinylphenol-*co*-methyl methacrylate) (PVPh-*co*-PMMA) with poly(vinylmethylketone) (PVMK) 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 Tg measurements were carried out at a heating rate of 20 °C/min under nitrogen flow and the Tg value was taken as the midpoint of the transition of the second scan.

Table 1.
Polymer characteristics.

Polymers	M_w	M_w/M_n	Tg (°C)
PVPhMMA50	150.000	1.84	135.8
PVMK	500.000	-	37.5

FTIR measurement was recorded on a Nikolet Avatar 6700 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/PVMK 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 1.

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 also important information about the physical state, morphology of these blends, and the possible relaxations that occur at the segments level during the transition.[6]

The differential scanning calorimetry (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. Moreover, it has been established that the observation of a single glass temperature transition (Tg) between those

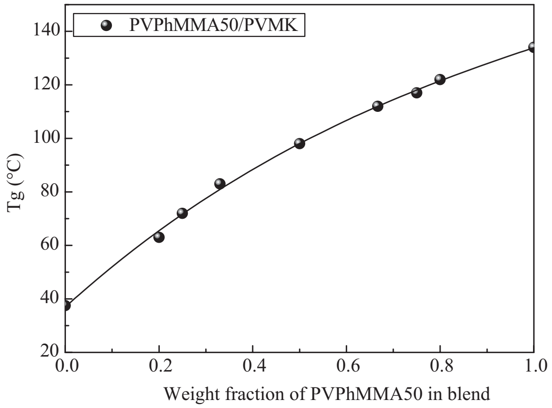

Figure 1.
Tg-Composition versus weight fraction of PVPhMMA50 in blend.

of the pure constituents is indicative of their miscibility. While the detection of the two Tǵs corresponding to the pure constituents of blend, indicating their immiscibility.[7]

Figure 1 displays the Tg-composition of blends of PVPhMMA5/PVMK. As can be seen in this figure, the single glass transition temperature (Tg) is observed for each composition can be considered as an evidence of the miscibility of these blends in all range composition. Thus, the positive deviation of Tg values from average of the glass transition of pure components revealing that this miscibility may be due to the presence of specific interactions occurring between the two polymers. In very recently, we have obtained similar results concerning the blends of poly(styrene-co-4-vinyl pyridine) (PS4VP30) copolymers with PVPhMMA50.[8]

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 this type of interactions. It is proven to be a powerful technique to study the specific interactions.[9–10] 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 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 phenol ring interactions is generally 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 PVPhMMA/PVMK using infra-red 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}. The general features of the obtained infrared spectra of pure PVPhMMA50 and PVMK, 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.[11]

Figure 2 shows a scale expanded FTIR spectra in the carbonyl stretching region (1650–1770 cm^{-1}) of PVPhMMA50, PVMK and their blends in different ratios. PVMK exhibits only one characteristic band localized at 1711 cm^{-1} assigned to free carbonyl, whereas the pure PVPhMMA50 shows two characteristic bands observed at 1728 and 1705 cm^{-1}. These bands are respectively attributed to free carbonyl stretching vibra-

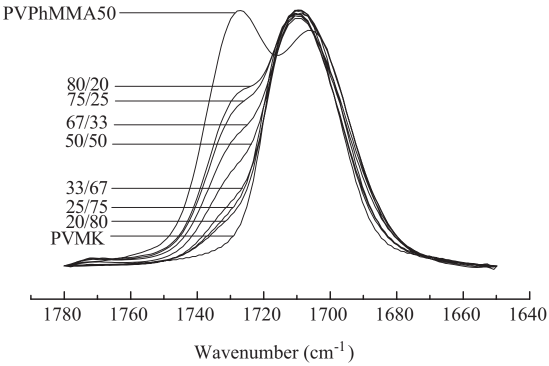

Figure 2.
FTIR spectra of PVPhMMA50, PVMK and their blends recorded at room temperature in the carbonyl stretching region.

tions (not hydrogen bonded) and to those that are self-associated (hydrogen bonded) with hydroxyl groups of VPh. When PVMK is added progressively in blend, it can be clearly observed that the relative absorbance of the free carbonyl stretching band showed at 1728 cm^{-1} of pure PVPhMMA50 decreases intimately with increasing of PVMK composition in blend and shifted slightly to a lower frequency. Also, the second band relative of the hydrogen bonded of carbonyl stretching band observed at 1705 cm^{-1} shifted slightly to a higher frequency (up to 1710 cm^{-1}). Therefore, we believe that the addition of PVMK in the blends affects the intra and/or interassociation hydroxyl-hydroxyl and enhanced the density of hydrogen bonding that could be occurred between hydroxyl and carbonyl groups. These results may be due to the preferential intermolecular interactions between unlike species resulting mainly from the broken of the hydrogen-bonded formed between phenolic hydroxyl groups of VPh. 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 and coworkers.[8,12]

Although, the carbonyl groups of PVMK and PVPhMMA50 absorb in same region, a quantitative analysis is rather difficult in this region. Therefore, we have used an appropriate curve fitting method an attempt to determine the evolution of the free carbonyl stretching of PVPhMMA50 when PVMK is added in the blend. The fractions of free, associated and liberated carbonyl of PVMK in blends are calculated and summarized in Table 2. It can be shown that the fraction of free carbonyl

Table 2.
Curve-fitting data from FTIR carbonyl band of PVPhMMA50/PVPMK blends.

	ν	$W_{1/2}$	f_{free}	ν	$W_{1/2}$	f_{Asso}	ν	$W_{1/2}$	f_{lib}
PVPhMMA50/ PVMK	cm^{-1}	cm^{-1}		cm^{-1}	cm^{-1}		cm^{-1}	cm^{-1}	
82/20	1728	22	0.731	1699	28	0.215	1710	25	0.054
75/25	1727	22	0.641	1699	28	0.289	1709	24	0.070
67/33	1728	21	0.558	1700	30	0.345	1710	24	0.097
50/50	1728	22	0.416	1700	32	0.408	1710	25	0.176
33/67	1729	20	0.339	1700	32	0.502	1709	25	0.159
25/75	1728	22	0.276	1700	29	0.545	1711	24	0.179
20/80	1728	22	0.270	1700	32	0.557	1710	23	0.173

Data obtained by fixing the positions and widths at half-height (ν, $W_{1/2}$ cm^{-1}) of free (1727, 22) and dimeric (1700, 29 cm^{-1}) carbonyls in the 1780–1650 cm^{-1} region.

of PVPhMMA50 decreases with the amount of PVMK in the blends, whereas the hydrogen bonding fraction decreases. In other words, this is indicative of the presence of specific interactions between PVPHMMA50 and PVMK.

Conclusion

In this work, the miscibility of PVPhMMA50 with a PVMK has been investigated by DSC, FTIR. This miscibility was firstly evidenced by DSC where a single Tg was detected for each composition of the blends. It has also been shown that the positive deviation of Tg values from average of the glass transition of pure components revealing that this miscibility may be due to the presence of specific interactions occurring between the two polymers. FTIR results also confirm the presence of these hydrogen bonding interactions qualitatively by the deceasing of the relative absorbance of the free carbonyl stretching band showed at 1728 cm^{-1} of pure PVPhMMA50 with increasing of PVMK in the blend. This is may be attributed to the new conformation of PVPhMMA50 that can allowed to increase the amount of hydrogen bonding between two polymers. This trend is confirmed quantitatively from the evaluation of the fraction of free carbonyl of PVPhMMA50 when PVMK is added in blends.

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