

Miscibility Study of Poly(vinyl chloride)/Poly(methyl methacrylate-co-4-vinylpyridine) by Viscosimetry, DSC, and FTIR

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ABSTRACT: The miscibility of the poly(vinyl chloride)/poly(methylmethacrylate) system were improved by introducing pyridine units into poly(methylmethacrylate) main. For this purpose, we have synthesized through a radical polymerization a series of methylmethacrylate-co-vinyl-4-pyridine copolymers of different compositions and carried out a comparative study by viscosimetry, differential scanning calorimetry, and Fourier transform infrared spectroscopic (FTIR) methods. The viscosimetric analysis using the Krigbaum-Wall, K. K. Chee, and Compos approaches revealed that, the Poly(vinyl chloride)/poly(methylmethacrylate-co-4-vinylpyridine)(PVC/MMA4VP-15) at 15 wt % of 4-vinylpyridine systems in tetrahydrofuran are completely miscible in all proportions. The differential scanning calorimetry analysis confirmed the miscibility of these systems in all proportions by the appearance of only one glass tran-

sition temperature between those of the two pure constituents. The Kwei and Schneider approaches showed also the miscibility of this system, which is due to the specific interactions between the acidic hydrogen atom of PVC and the nitrogen of MMA4VP-15. The use of FTIR method has confirmed the occurrence of this kind of interactions by broadening and shifting of the involved functional groups vibration bands. In this work, we have also carried out a preliminary test of sorption of THF aqueous solution by PVC and PVC/MMA4VP-15 blend membranes. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 173–182, 2011

Key words: miscibility; poly(vinylchloride); poly(methylmethacrylate-co-4-vinylpyridine); hydrogen bond; viscosimetry; differential scanning calorimetry; Fourier transform infrared

INTRODUCTION

The use of polymers in a miscible mixture state constitutes an economic technique which enhances in certain cases the improvement of polymer material properties. However, it is well known that, in most cases the polymer mixtures are not miscible, so in this fact, the resulting mechanical properties are not desirable. It was reported that the poly(vinyl chloride) (PVC) is not miscible with several polymers.^{1,2} Several studies based on either the mixtures of PVC and polymethacrylates or polyacrylates, which are miscible in certain proportions, have shown a performance in different domains.^{3–8} In those investigations, it was noted that the rigidity, grinding, and extrusion of PVC have been particularly improved. PMMA is generally blended with PVC to improve the viscoelastic properties. Recently, Ahmad et al.⁹ have investigated on the stability of PVC. They con-

cluded that the stabilization effect on PVC was found mostly significant with 10 wt % PMMA matrix. Other investigations concerning the poly(vinylchloride)/poly(methylmethacrylate) (PVC/PMMA) blend have shown that this system became immiscible beyond 70% weight of PMMA.^{10–15} Deshpande et al.,¹⁶ however, have shown by thermal studies that the blends cast from methylethylketone were immiscible for 50 wt % of PVC. Aouachria et al.^{17,18} performed melt mixing of PVC and PMMA at 175°C. They have shown that these blends were miscible up to 60 wt % of PMMA. Other blends formed from PVC and copolymers have been also investigated by different authors.^{3–7} They showed that the insertion of basic groups within the polymeric main chains as copolymers seemed to improve appreciably the miscibility of certain polymers. The stabilization effect on PVC was found mostly significant with 10 wt % PMMA in the PVC matrix.

Concerning the poly(vinyl chloride)/poly(butylmethacrylate)(PVC/PBMA) mixture, the study carried out in our laboratory has shown that the insertion of 10–26 mol % of 4-vinyl-pyridine(4VP) groups in PBMA main chain improved the

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miscibility of the mixture.¹⁰ In this case, the substitution of some butylmethacrylate (BMA) ester groups by the pyridine groups within PBMA chains favored the development of acid-base interactions with PVC.

To improve the miscibility of PVC/PMMA system, we have synthesized, through free radical polymerization, a series of methylmethacrylate-*co*-4-vinylpyridine copolymers (MMA4VP-7, MMA4VP-15, and MMA4VP-21) containing 7, 15, and 21 wt % of 4VP respectively and carried out a comparative study using viscosimetry, differential scanning calorimetry, and FTIR spectroscopy.

In our future investigations this compatible blend will be applied as membrane of pervaporation for the extraction the organic effluents as THF and dioxane from water. In this fact, the Ray et al.¹⁹ investigations recently proved that the PVC used as membrane alone or mixed with other polymers gave a high performance in flux rate and selectivity. On the other hand, it is well known that the mechanical properties of PMMA do not permit the formation of the membranes for pervaporation, but according to the work of Susheelkumar et al.,²⁰ its modification by copolymerization or mixed with other polymers leads to excellent permselective membranes for extraction of dioxane from water. To reach this objective we are concluded this investigation by a preliminary test of sorption of THF by PVC/MMA4VP-15 membranes.

EXPERIMENTAL

Materials

The solvents and the precipitants such as: chloroform, tetrahydrofuran (THF), heptane, and petroleum ether (Aldrich, 99% purity) were used without further purification. Azo-bis-isobutyronitrile (AIBN) (Aldrich, 98% purity) was purified by recrystallization in methanol. The monomers, methylmethacrylate (MMA), and vinyl-4-pyridine (V4P) (Aldrich, 98% purity) were distilled under inert atmosphere and kept at -20°C . The poly(vinyl chloride) with K value 67, kindly supplied by Industrial Complex of Skikda, Algeria, was purified by dissolution in tetrahydrofuran (THF) and precipitated out with petroleum ether. The polymer blend PVC/MMA4VP was prepared in four mass ratios (30 : 70, 50 : 50, 70 : 30, 80 : 20) by coprecipitation from THF solutions in an excess of petroleum ether. The blends were dried in a vacuum oven at 60°C for several days.

Polymerization and copolymerization

The polymerization of MMA and its copolymerization with V4P were prepared by free radical solution

TABLE I
Synthesis of Polymethylmethacrylate (PMMA) and Copolymers (MMA4VP) at Different Compositions

Polymer	AIBN (g)	MMA (g)	4VP (g)	Yield (%)
PMMA	0.135	135	–	17
MMA4VP-7	0.02	18	2	10
MMA4VP-15	0.02	16	4	13
MMA4VP-21	0.02	4	16	14

polymerization using AIBN as initiator in THF at 60°C during 90 min. The polymers and copolymers were purified by repeated dissolution in THF and precipitation in heptane then isolated by filtration and dried to a constant weight at 40°C in a vacuum oven for several days. Table I illustrates the polymerization and copolymerization at different compositions.

Preparation of PVC and PVC/MMA4VP-15 membranes

The polymers, copolymers or their blends were dissolved at 10 wt % in THF. The polymer membrane was prepared by smoothly spreading polymeric solution over a teflon-plate surface. The plate was then heated at 40°C for 3 days and dried under vacuum at 50°C for 24 h. The thickness of each membrane was about 50 μm .

We have noted that the mechanic properties of MMA4VP-15 alone did not permit the formation of flexible membranes and so binding with PVC is necessary.

Swelling measurements and sorption experiments

The dried membrane with known weight was immersed into THF/water mixtures with 10% THF at 30°C for 24 h. When the sample kept a constant weight, it was carefully blotted between filter papers to remove surface liquid, and then weighed quickly to measure the weight of the swollen membrane. All experiments were repeated at least three times, and the results were averaged. In the sorption experiments, the liquid sorbed in membranes was recovered in a liquid nitrogen trap by desorbing the equilibrated sample in the purge-and-trap apparatus similar at those detailed by Lianyu et al.²¹

Characterization

The compositions of the 4VP comonomer units in the copolymers were determined by UV-Spectrometric method at 257 nm in chloroform by using a Shimadzu 12,001 spectrophotometer UV-visible. The description of the used method of measurement was

similar to those detailed in an earlier publication²² using the poly(4-vinylpyridine) as standard. It was found that MMA4VP-7, MMA4VP-15, and MMA 4VP-21 contained respectively 7, 15, and 21 wt % of 4VP.

The glass transition temperature of the pure components and blends was measured with a differential scanning calorimeter (DSC; Setaram Labsys DSC 16), previously calibrated with indium, at 20°C/min rate. The samples of 10–15 mg were preheated to 200°C under nitrogen atmosphere and kept at that temperature for 10 min to ensure total elimination of solvent. The data were collected from the second and third scan. No degradation phenomenon of PVC and PVC/MMA4VP blends was observed in all thermograms, This is also confirmed by a test of solubility and NMR spectroscopy analysis conducted after DSC analysis. The glass transition temperature was taken as the midpoint in the heat capacity change with temperature.

The reduced viscosity measurements of PVC, PMMA, copolymers MMA4VP and their mixtures were conducted at 25°C in THF using a viscosimeter Ubbelohde Scott Gerate type Avs 310. It was noted that the viscosimetric average molecular weights \bar{M}_v of PVC, PMMA, and MMA4VP copolymers were 4.2×10^4 , 6×10^4 and around 10^5 g/mol, respectively.

The description of the used technique and methods of measurement have been detailed by Soria et al.²³ The specific and intrinsic coefficients of viscosity of each polymer or copolymer, in the chloroform/polymeric solute binary, or chloroform/copolymer/polymer ternary systems, have been determined by infinite-dilution extrapolation of the copolymer with the chloroform/polymer binary mixture, i.e., if the system is named solvent (S)/copolymer(Cx)/polymer(P), the values of the intrinsic coefficient of viscosity of copolymer (Cx) in a dilute solution of polymer (P) are obtained by zero-concentration extrapolation of Cx in a binary mixture, in which the concentration of P is constant.

The IR spectra were recorded by a GENESIS II FTIR spectrometer at ambient temperature. In all cases, at least 32 scans with an accuracy of 1 cm^{-1} were signal-averaged. The THF solution containing the blend was cast onto NaCl disk and dried at 60°C for 4 h. The film used in this study was sufficiently thin to obey the Beer-Lambert law. For qualitative and quantitative studies the spectra were analyzed by Grams 386 program.

The liquid sorbed was analyzed by gas chromatography using Shimadzu-14B with the following parts: TCD detector (katharometer), N_2 as a carrier gas, Carbowax 20M as a stationary phase, column (2 m in length, 3.17 mm in diameter); injection-port temperature, 130°C; column temperature, 180°C; detector temperature, 180°C.

CALCULATIONS

Determination of viscosimetric interaction parameters

To determine the viscosimetric parameters of a ternary system composed of a solvent(1) and two polymers(2) and (3) at different proportions, we have resorted to the following three approaches.

Krigbaum-Wall approach

According to Krigbaum-Wall,¹¹ the specific viscosity (η_{sp}) of polymers mixture is given by the relationship:

$$\frac{(\eta_{sp})_m}{C_m} = [\eta]_m + b_m C_m \quad (1)$$

with

$$b_m^{\text{exp}} = W_2^2 b_{22} + W_3^2 b_{33} + 2W_2 W_3 b_{23}^{\text{exp}}$$

and

$$(\eta_{sp})_m = [\eta]_2 C_2 + [\eta]_3 C_3 + b_{22} C_2^2 + b_{33} C_3^2 + b_{23}^{\text{exp}} C_2 C_3 \quad (2)$$

where W_i , $[\eta]_i$ and C_i are respectively the weight fraction, intrinsic viscosity, and concentration of polymer (i) in the mixture; b_m , b_{ii} , b_{jj} , and b_{ij}^{exp} are respectively the global interaction parameters between the two polymers, the viscosimetric interaction between the polymer (i) and the solvent, the polymer (j) and the solvent and experimental between the two polymers (i) and (j). We note that:

$$b_{ii} = k_i [\eta]_i^2 \quad (3)$$

where k_i is the Huggins coefficient.

The theoretical interaction parameter between the two polymers is given by the following equation:

$$b_{23}^{\text{the}} = (b_{ii} \cdot b_{jj})^{\frac{1}{2}} \quad (4)$$

According to the approach proposed by Krigbaum-wall, a mixture of two polymers is miscible when the difference Δb_{23} is positive.

K. K. Chee approach

The K. K. Chee approach¹² is based on the evaluation of the ΔB determined by the expression:

$$\Delta B = \frac{b_m - \bar{b}}{2W_2 W_3} \quad (5)$$

with

$$\bar{b} = W_2 b_{22} + W_3 b_{33}$$

According to this approach, the miscibility of two polymers is considered when $\Delta B \geq 0$.

Compos approach

To predict the miscibility of a pair of polymers in solution, Compos¹³ has proposed two criteria:

The first criterion is based on the calculation of an ideal interaction parameter given by the following equation:

$$b_m^{(id)} = b_{22}W_2^2 + b_{33}W_3^2 \quad (6)$$

where

$$\Delta b_m = b_m - b_m^{(id)} \quad (7)$$

The polymers system is miscible when $\Delta b_m > 0$, and it is not miscible in the reverse case.

The second criterion is based on the comparison between the theoretical value of intrinsic viscosity $[\eta]^{th}$ and its experimental value $[\eta]^{exp}$:

$$\Delta[\eta] = [\eta]^{exp} - [\eta]^{th} \quad (8)$$

and

$$[\eta]^{th} = [\eta]_2 W_2 + [\eta]_3 W_3 \quad (9)$$

The negative values of $\Delta[\eta]$ characterize the miscible mixtures.

The study by DSC

To confirm the existence of intermolecular interactions between the constituents of the mixture, we are applied the two following approaches:

Fox approach

The relationship which links $T_g(m)$ to $T_g(2)$ and $T_g(3)$ according to Fox¹⁴ is given by the following equation:

$$\frac{1}{T_g(m)} = \frac{W_2}{T_g(2)} + \frac{W_3}{T_g(3)} \quad (10)$$

$T_g(m)$, $T_g(2)$ and $T_g(3)$ are the glass transition temperatures of the mixture, polymer (2) and polymer (3) respectively.

The deviation of experimental T_g values compared with those calculated by Fox equation is attributed

to the absence of the term, due to the specific interactions between the constituents of the mixture.

Schneider approach

Schneider et al.²⁴ established an equation to confirm the existence of specific interactions between the constituents of the mixture.

$$\frac{T_g(m) - T_g(2)}{[T_g(3) - T_g(2)]W_{3C}} = (1 + K_2) - (K_2 + K_3)W_{3C} + K_3W_{3C}^2 \quad (11)$$

where

$$W_{3C} = \frac{KW_3}{W_2 + KW_3} \quad \text{and} \quad K = \frac{\rho_2 T_{g2}}{\rho_3 T_{g3}}$$

W_{3C} , is the corrected weight fraction of constituent (3) which has the higher glass transition temperature and K is the constant. ρ_2 and ρ_3 , are respectively the density of polymer (2) and polymer (3).

K_2 and K_3 are the constants proportional to the intensities of the molecular interaction, depending on the orientation effects. The former is thermodynamically favorable to the miscibility and highlights the contribution of heterogenic interaction, whereas the latter is due to the conformational entropy effects of the mixture.

For the systems devoid of any specific interaction:

$$K_2 = K_3 = 0$$

so

$$\frac{T_g(m) - T_g(2)}{[T_g(3) - T_g(2)]W_{3C}} = 1 \quad (12)$$

This equation indicates that all positive deviations compared with the horizontal straight line from the origin to the ordinate equal to 1 are considered to highlight the specific interactions between the constituents of the mixture.

The study by infrared spectrometry

The use of FTIR spectrometry technique allows to study qualitatively a mixture of polymers by comparing the spectra of pure constituents with those of their mixtures.²⁵⁻²⁷ In fact, in case of miscibility, the differences between the spectra are explained by a shift, broadening, intensity reduction and/or the appearance of new bands.

This technique also allows to estimate quantitatively the specific interactions of hydrogen bonds using the deconvolution method based on the

TABLE II
Qualitative Tests of Miscibility and Complexation of
PVC/MMA4VP System at Different Compositions in
THF at 25°C

Mixture	Composition	Observation
PVC/MMA4VP-7	30/70	Miscible
	50/50	Miscible
	70/30	Miscible
	80/20	Miscible
PVC/MMA4VP-15	30/70	Miscible
	50/50	Miscible
	70/30	Miscible
	80/20	Miscible
PVC/MMA4VP-21	30/70	Complex
	50/50	Complex
	70/30	Complex
	80/20	Complex

calculation of three groups fractions (associated and not associated). It was reported in the literature that the shift of the absorption band of the carbonyl towards the lower wavelength numbers reflects the existence of specific interactions of hydrogen bonds.²⁸⁻³⁰

Other investigations reported on the PVC/PBMA mixture have shown that the miscibility in this mixture is attributed to the specific interactions involving between the acid hydrogen of PVC and the ester group of PBMA.¹⁰ In fact, a shift of 2 cm^{-1} of the ester band is noted, in addition to a broadening of this band.

Swelling measurements and sorption experiments

The degree of swelling (S) for the membrane is defined by

$$S(\%) = \frac{w_s - w_d}{w_d} \times 100 \quad (13)$$

where w_d and w_s are the weights of dry and swollen membranes, respectively.

The sorption selectivity, α_{THF} , can be expressed as

$$\alpha_{\text{THF}} = \frac{f_{\text{THF}}/f_{\text{H}_2\text{O}}}{F_{\text{THF}}/F_{\text{H}_2\text{O}}} \quad (14)$$

where F_{THF} and $F_{\text{H}_2\text{O}}$ are weight fractions of THF and water in feed solution and f_{THF} and $f_{\text{H}_2\text{O}}$ are those in membranes, respectively.

RESULTS AND DISCUSSION

According to the preliminary tests of PVC/PMMA system, the observation of one phase relatively concentrated and a transparent film obtained after solvent evaporation was an indication of the miscibility. This result was observed at concentrations lower

than 70% weight of PMMA in the mixture. On the contrary at higher concentrations, two phases in equilibrium were observed indicating that the system was in heterogenic state, and the mixture was partially miscible. These observations confirm the results obtained by different authors using the DSC and FTIR methods.¹⁰⁻¹⁸

Concerning the two systems PVC/PMMA4VP-15 and PVC/PMMA4VP-7, only one phase and a transparent film were observed in the mixtures for all compositions.

Moreover, for other blends, several studies³¹⁻³⁴ have shown that the progressive rise of interactional sites between the constituents permit to observe the non miscibility-miscibility and miscibility-complexation transitions.

Concerning the PVC/PMMA4VP-21 blend we was observed the formation of an interpolymer complex, in this case, the polymers seems develop strong intermolecular interactions, leading to an associative separation of the two phases; one of them is concentrated and contains the majority of the two polymers (2) and (3) (strong intermolecular interactions) in equilibrium with a very dilute phase (weak intermolecular interactions). This phenomenon was also observed by other author using similar systems.³⁵ We have noted in PVC/PMMA blend that the difference between the solubility parameters of its constituents is $6.5 [(\text{k}\cdot\text{m}^{-3})^{0.5}]$ ¹¹ so that miscibility resulted from the existence of intermolecular interactions bonding. The qualitative solubility tests of the synthesized copolymers have shown that the products are soluble in THF.

The qualitative tests of miscibility or complexation of PVC/PMMA4VP mixtures at different concentrations of V4P in THF are revealed on the results grouped in Table II. The miscibility of PVC/PMMA4VP-7 and PVC/PMMA4VP-15 in all proportions was proved by the formation of one phase in THF at ambient temperature. This shows the role played by the intermolecular interactions of hydrogen bonds existing between the constituents of each mixture. Similar interactions was considered by different authors as specific.³⁶⁻⁴¹

In the particular case of PVC/PMMA4VP-21, we have noted a coprecipitation of the two polymers in THF, due to the presence of strong hydrogen bond interactions in the mixtures compared with the other two systems. These interactions lead to the formation of intermolecular complexes.

We can conclude from the qualitative tests that the progressive increase of basic comonomer 4VP in the main chains of PMMA creates a rise in the number of functional groups belonging to several available chains. That rise develops more intermolecular interactions due to hydrogen bonds which become more and more intense between the acid hydrogen

TABLE III
Viscosimetric Interaction Parameters Obtained at 25°C in THF According to Krigbaum Wall and K. K. Chee Approaches

Mixture PVC/MMA4VP-15	b (dl/g) ²	Δb_{23} (dl/g) ²	b_{23}^{th} (dl/g) ²	b_{23}^{exp} (dl/g) ²	ΔB (dl/g) ²
80/20	0.147	0.0069	0.178	0.184	0.022
70/30	0.158	0.0095	0.178	0.188	0.018
50/50	0.181	0.0067	0.178	0.185	0.009
0.006	0.204	0.0076	0.178	0.186	0.006

of PVC and the nitrogen of pyridine groups of these mixtures. Consequently, this fact leads to the transition from an immiscible system to a miscible system and from a miscible system to an interpolymer complex.

Concerning the PVC/MMA4VP-7 blend and because of the low quantity V4P unit incorporated in PMMA main chain (7 wt %), we could not easily evaluate with acceptable precision its effects by using Viscosimetry and FTIR methods. So we are satisfied in this system with only DSC and the preliminary test. We have focused in this study our effort only on the PVC/MMA4VP-15 blend as an typical example.

The studies of the miscibility by viscosimetry

Figure 1 represents the variation of the reduced viscosities versus the concentration of PVC/MMA4VP-15 system in THF. The curves show a linearity indicating the miscibility of this mixture, and invalidity of all complexation in this ternary mixture. Similar results have been observed by Kulshreshatha et al.⁴² using the mixture of PVC and terpolymer(acrylonitrile/butadiene/styrene).

The intrinsic viscosities of PVC/MMA4VP-15 mixtures at compositions 80 : 20, 70 : 30 and 50 : 50 are weaker than their pure constituents, while the viscosity of 30 : 70 is between the values of the two pure constituents. Such behavior may be explained by the predominance of heterogeneous contacts (segments of polymer(*i*)-segment of polymer (*j*) of different type), on the homogeneous contacts [segments of polymer(*i*)-segment of polymer (*j*) of the same type], which are hydrogen bonds. Conversely, the PVC/

MMA4VP-15 mixture at a composition of 30 : 70 shows a straight line with a positive slope and an intermediary intrinsic viscosity between those of the pure constituents. A similar behavior was observed by Cherifi et al.⁴³ using the poly(styrene-*co*-acrylonitrile)/poly(styrene-*co*-cinnamic acid) mixture.

Determination of viscosimetric interaction parameters

The experimental parameters (b_{23}^{exp}), the theoretical values (b_{23}^{th}) and their differences (Δb_{23}) were determined according to the Krigbaum-Wall approach and are listed in Table III. Through these results, we have noted that the PVC/MMA4VP-15 system is perfectly miscible in all proportions since the values of Δb_{23} are positive in all domain of compositions.

The results of the theoretical predictions obtained using the K. K. Chee approach are listed in Table III. From these values, we deduce that the PVC/MMA4VP-15 mixture at different compositions is miscible because the difference ΔB is positive.

Table IV illustrates the results of Δb_m obtained by the Compos equation. According to the first criterion of Compos, the PVC/MMA4VP-15 mixture is miscible because the value of Δb_m is positive in all proportions. The positive values of Δb_m explain the existence of intermolecular interactions due to hydrogen bond between the different chains. According to the second criterion, the negative values of $\Delta[\eta]$ also indicate that the studied mixture is miscible. As shown in Figure 2, the increase of the basic groups in the main chain of polymers leads to a perfect miscibility of the mixture system. In this way, we have

TABLE IV
 $b_m^{(id)}$ and Δb_m Values, for PVC/MMA4VP-15 System, Obtained According Compos Approach and Experimental, Theoretical Intrinsic Viscosities and Their Differences Obtained at 25°C

System	$[\eta]^{\text{th}}$	$[\eta]^{\text{exp}}$	Δb_m	$b_m^{(id)}$	$\Delta[\eta]$
100/0	–	0.589	–	–	–
80/20	0.598	0.751	0.065	0.089	–0.093
70/30	0.603	0.403	0.083	0.082	–0.132
50/50	0.613	0.590	0.095	0.090	–0.209
30/70	0.622	0.635	0.079	0.128	–0.032
0/100	–	0.635	–	–	–

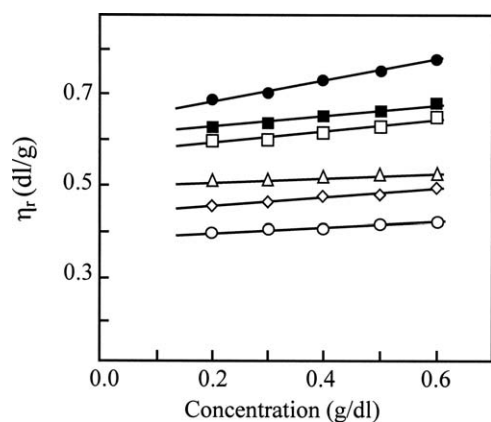


Figure 1 The viscosimetric curves of PVC/ PVC/ MMA4VP-15 blend at different compositions in THF at 25°C. (□) PVC; (●) MMA4VP-15; (◇): 80/20; (Δ) 70/30; (○) 50/50; (■) 30/70.

observed a negative deviation of the experimental intrinsic viscosity compared to the theoretical values.

The study by DSC

The DSC thermograms of the pure constituents, PVC, MMA4VP-15 and their mixtures at different compositions are shown in Figure 3 while the glass transition temperatures values (T_g) of pure polymers, copolymers and their blends are listed in Table V. The observation of only one T_g on the thermograms of all mixtures confirms the miscibility of PVC/MMA4VP-15 and PVC/MMA4VP-7 systems.

The variation of T_g in these mixtures with the composition of MMA4VP-15 and MMA4VP-7 shows a positive deviation compared with the average arithmetical T_g value of the pure constituents. This fact reflects, according to Kwei approach,⁴⁴ the presence of intermolecular interactions of hydrogen bonding

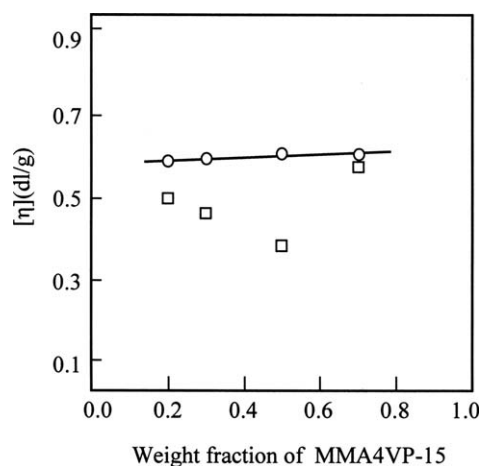


Figure 2 Variation of experimental and theoretical intrinsic viscosity versus the concentration of MMA4VP-15 in the mixture. ○, theoretical intrinsic viscosity; □, experimental intrinsic viscosity.

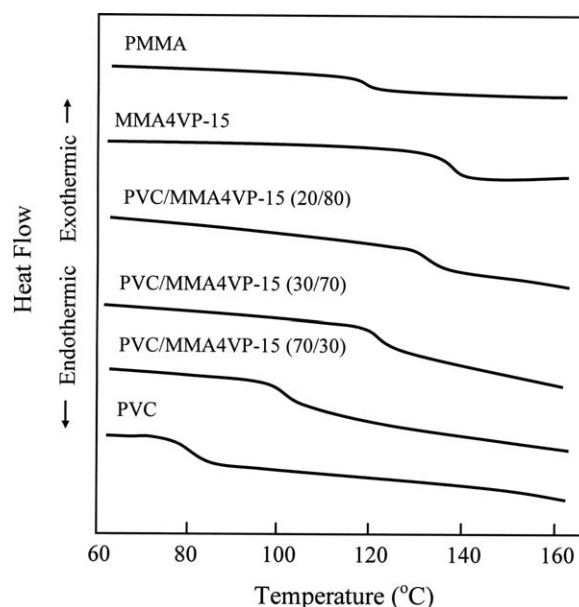


Figure 3 DSC thermograms of PVC, PMMA, MMA4VP-15, and those of their blends at different compositions.

type. These interactions reduce the free volume and mobility of the polymer chains and lead, by this way, to a rise in the T_g values.

According to the results of Table V we have observed that the values of the glass transition temperatures of the mixtures $T_{g(m)}$ calculated from the Fox equation wander from those measured experimentally. This deficiency is attributed to the absence of a term reflecting the role played by the intermolecular interactions between the constituents of the mixtures.

Table VI recapitulates the variation of the first term value of Schneider equation $[T_{g(m)} - T_g(2)]/[T_g(3) - T_g(2)] \cdot W_{3c}$ versus the corrected weight fraction W_{3c} of the two systems. These results reveal a positive deviation compared with a horizontal straight line an ordinate equal to 1 and confirm

TABLE V
Experimental Glass Transition Temperatures (T_g) of PVC, MMA4VP-15, MMA4VP-7 and Their Mixtures at Different Compositions Obtained Experimentally and According to the Fox Equation

System	T_g (exp.) (°C)	T_g (Fox) (°C)
PVC	81	–
PMMA	117	–
PVC/MMA4VP-15		
0/100	138	–
20/80	133	120
30/70	120	114
70/30	109	93
PVC/MMA4VP-7		
0/100	131	–
20/80	125	117
30/70	118	111
70/30	96	91

TABLE VI
 $[T_g(m)-T_g(2)]/[T_g(3)-T_g(2)]W_{3c}$ Values for PVC/MMA4VP-15 and PVC/MMA4VP Systems

System	W_2	W_3	W_{3c}	$\frac{T_g(m)-T_g(2)}{[T_g(3)-T_g(2)]W_{3c}}$
PVC/MMA4VP				
20/80	0.2	0.8	0.775	1.198
30/70	0.3	0.7	0.668	1.302
70/30	0.7	0.3	0.270	1.739
PVC/MMA4VP-7				
20/80	0.2	0.8	0.712	1.236
30/70	0.3	0.7	0.590	1.254
70/30	0.7	0.3	0.210	1.428

thus, the existence of interactions between the two polymeric constituents.

The study by FTIR

The results of copolymer MMA4VP-15 obtained by IR analysis in Figure 4(a) have shown a shift of the carbonyl bond towards the higher wavelength numbers (1765 cm^{-1}) compared with the pure PMMA spectrum (1730 cm^{-1}). This shift reflects the disruption of PMMA polymeric chains by the V4P basic comonomer and explains the existence of repulsive interactions between the ester and pyridine groups.

The intermolecular interactions highlighted by FTIR spectroscopy in PVC/MMA4VP-15 at different compositions are reflected by the broadening and

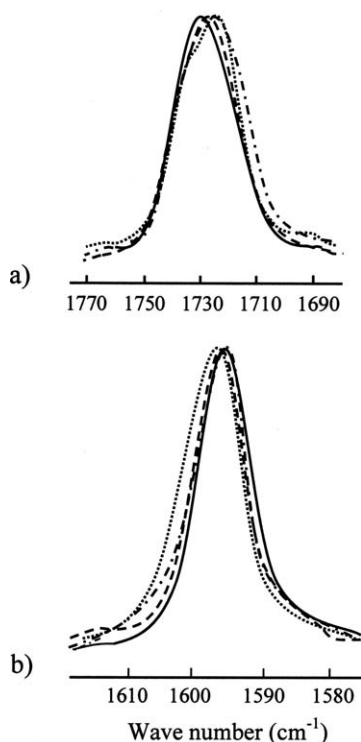


Figure 4 The normalized spectra of PVC/MMA4VP-15 system at different compositions in: (a) $1765\text{--}1690\text{ cm}^{-1}$ region; (b) $1620\text{--}1575\text{ cm}^{-1}$ region. (—): 0/100; (---):30/70; (-·-·):50/50 and (····):70/30 (wt %).

shifting of the carbonyl bond toward the lower wavelength numbers, as illustrated in Figure 4(a). This latter effect is attributed to the interactions between the carbonyl and acid hydrogen of PVC as showed in the Scheme 1. Similar results were also obtained in PVC/PMMA⁹ and in PVC/BMA4VP systems.¹⁰ When the chains of MMA4VP are diluted in excess of PVC, the hydrogen of PVC develops interactions with the ester and/or pyridine groups as it occurs in the MMA4VP-15 copolymer chains as showed in the Scheme 1.

A shift of the bonds ($2\text{--}5\text{ cm}^{-1}$) is observed when the weight fraction of PVC in the mixture increases [Fig. 4(a)]. These observations confirm qualitatively the existence of intermolecular interactions of hydrogen bonding within the PVC/MMA4VP-15 system.

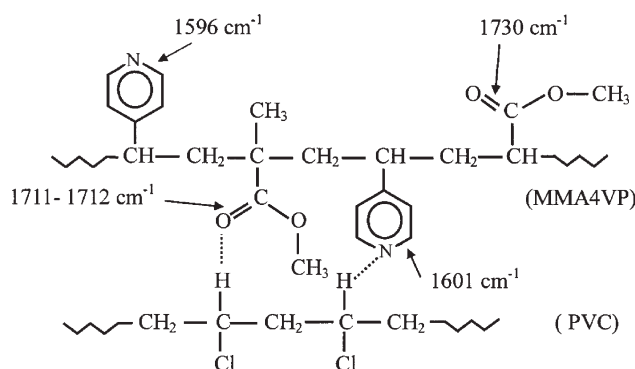
The data processing of the spectra by deconvolution highlights the presence of one peak around 1711 cm^{-1} . This is attributed to the carbonyl interacting with the acid hydrogen of PVC. The fractions of the free and associated carbonyls have been calculated by the following relationship:⁴⁵

$$F_1 = \frac{A_1}{A_1 + A_a \varepsilon} \quad (15)$$

where A_a and A_1 are respectively the relative areas of the associated and free carbonyl bonds; ε is the absorptivity fraction of the two previous bonds, and in case of carbonyls ε is equal to 1.1.⁴⁶

The deconvolution results of the PVC/PMMA4VP-15 system spectra in the carbonyl domain are grouped in Table VII and allow to calculate the fractions of free and associated carbonyls.

In the absorption domain of pyridine, the miscibility of PVC/MMA4VP-15 system is essentially attributed to the intermolecular interactions between the acid hydrogen of PVC and either ester or pyridine. The insertion of basic comonomer 4VP within PMMA allows the substitution of the carbonyl acceptor sites by pyridine groups and consequently the formation of hydrogen bonds with PVC. The spectral analysis of



Scheme 1 Hydrogen bond association in PVC/MMAVP blends.

TABLE VII
Deconvolution of Carbonyl Bands in 1765–1690 cm^{-1} and Pyridine Group Bands in 1620–1575 cm^{-1} Regions of PVC/MMA4VP-15 System

System (wt %)	Carbonyl associated		Carbonyl free		F_1	Pyridine associated		Pyridine free		F_1
	Width of peak $w(\text{cm}^{-1})$	Wavelength number $v(\text{cm}^{-1})$	Width of peak $w(\text{cm}^{-1})$	Wavelength number $v(\text{cm}^{-1})$		Width of peak $w(\text{cm}^{-1})$	Wavelength number $v(\text{cm}^{-1})$	Width of peak $w(\text{cm}^{-1})$	Wavelength number $v(\text{cm}^{-1})$	
30/70	27	1712	22	1730	0.86	9	1601	9	1596	0.36
50/50	29	1712	24	1730	0.84	8	1601	10	1596	0.76
70/30	32	1712	25	1730	0.78	7	1601	9	1596	0.84

the same system in the 1620–1575 cm^{-1} domain [Fig. 4(b)] shows a shift of the band centered at 1596 cm^{-1} toward higher wavelength numbers. This observation is attributed to the pyridine-acid hydrogen of PVC interactions which become more and more intense when the PVC is in excess.

A quantitative study of PVC/MMA4VP-15 spectra at different compositions in the absorption domain of pyridine was carried out from the same relationship previously used in the carbonyls domain, with ϵ equal to 1.

The calculated fractions of the free and associated pyridine are listed in Table VII.

Figure 5 illustrates the results obtained by smoothing FTIR spectra of PVC/MMA4VP-15 mixture at 50 : 50 and 70 : 30 compositions in the 1620–1575 cm^{-1} region. However, the values corresponding to the free pyridine fractions obtained can be explained by the limited

rate of 4VP used. Nevertheless, this amount was sufficient for improving the miscibility of PVC/PMMA system which is considered to be partially miscible.

The study of swelling and sorption behavior of PVC and PVC/MMA4VP-15 blends

The swelling performance of PVC, PVC/MMA4VP-15 blend membranes with THF aqueous solution can be deduced from the diagram in Figure 6. This diagram shows clearly that the amount of THF aqueous solution absorbed in membrane increased with increasing the composition of MMA4VP-15 in the blend. A four-fold increase of the PVC membrane weight occurs after 24 h when incorporated with 70 wt % MMA4VP-15, whereas, When using a membrane contained 30 wt % of MMA4VP, the sorption selectivity reach the maximum at 65 corresponding at about 70 wt % of THF absorbed. This can be explained by increasing of the hydrophobicity of the membrane with increasing the composition of MMA4VP in the blend. These preliminary results are an indication for the promising application of this material as membrane for extraction of organic effluents such as THF and dioxane from water.

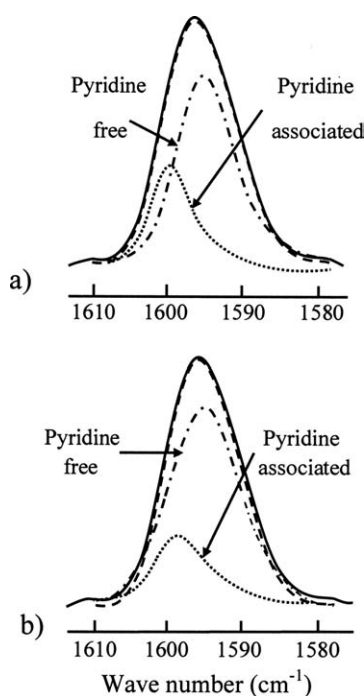


Figure 5 Smoothing of FTIR spectra of PVC/MMA4VP-15 system at: (a) 50/50 (wt %), and (b) 70/30 (wt %) compositions in 1620–1575 cm^{-1} region. (—) crude spectra; (---) smoothed spectra.

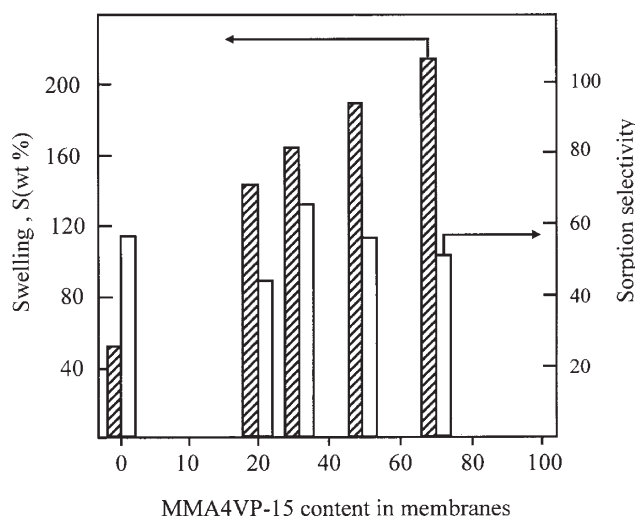


Figure 6 Effect of MMA4VP-15 content in membranes on the degree of swell and sorption selectivity for THF/water mixtures with 10% THF through the membranes at 30°C.

CONCLUSIONS

The insertion of the basic groups in PMMA were used to improve the miscibility of PVC and PMMA polymers. The viscosimetric study using Krigbaum-Wall, K. K. Chee and Compos approaches have revealed that PVC and MMA4VP-15 in THF are completely miscible in all proportions. The DSC showed the miscibility in all proportions of the same system by the presence of only one glass transition temperature, intermediate between those of the two pure constituents. By using the Kwei and Schneider approaches, this technique also allowed to confirm the miscibility of the system by the existence of specific interactions between the acid hydrogen of PVC and the nitrogen of MMA4VP-15. The interpretation of FTIR spectra confirmed the presence of the interactions between the two constituents of the mixtures by shifting and broadening of the vibration bands of the functional groups. The incorporation of MMA4VP-15 in PVC membrane favors increasing of the swelling degree of THF aqueous solution and conserve practically the same sorption selectivity. Finally, the use of PVC/MMA4VP compatible blend as membrane of pervaporation can be promising if employed for extraction of THF from water.

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