

Miscibility Enhancement on the Poly(vinylchloride)/Poly(methylmethacrylate) Blend and Characterization by Inverse Gas Chromatography: The Corrected Polymer–Polymer Interaction Parameters from the Probes Dependency

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ABSTRACT: The miscibility of poly(vinyl chloride)/poly(methylmethacrylate) (PVC/PMMA) system was improved by introducing some pyrrolidone units into the main chains of PMMA. For that purpose, we have synthesized two copolymers of poly(methylmethacrylate-*co*-vinylpyrrolidone) (MMVP) through a radical polymerization and carried out a comparative study of PVC/MMVP blends by inverse gas chromatography (IGC) and differential scanning calorimetry (DSC) methods. The adequacy of seven *n*-alkane probes has been tested to determine the thermodynamic parameters. The miscibility of the two systems has been proved by a single T_g for each blend. This observation was also confirmed by DSC analysis. To highlight the presence of interaction and its intensity between

PVC and MMVP in the blends, the polymer–polymer interaction parameters have been evaluated by IGC through which the influence of the solute has been resolved. The Schneider approach confirmed the miscibility of these systems as the K deviates positively from unity. The miscibility has been appeared highlighted from the positive difference in surface energy between the pure polymers and their blends. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1464–1474, 2012

Key words: poly(vinylchloride); poly(methylmethacrylate-*co*-vinylpyrrolidone); miscibility; corrected interaction parameters; inverse gas chromatography; differential scattering calorimetry

INTRODUCTION

The miscibility of poly(vinyl chloride) (PVC) with poly(*n*-alkylmethacrylate) has been studied by several investigators.^{1–21} The miscibility of these blends are complicated or complex depending on the molecular weight, microstructure of each constituent and preparation method of the blend. Poly(vinylchloride)/poly(methylmethacrylate) (PVC/PMMA) blends were also reported to adopt a variety of miscible blends. Several studies of the mixture of PVC and polymethacrylates or PVC and polyacrylates have shown a different performance in different domain on the basis of their miscibility in certain proportions in the blend.^{1–7} It has been noted that, the rigidity, grinding, extrusion of PVC, and the thermal stability have been particularly improved. PMMA is generally blended with PVC to improve

the viscoelastic properties. Recently Ahmad et al.⁷ have investigated on the stability of PVC using the PMMA as additives, it has been concluded that the stabilization effect on PVC was found to be significant with 10 wt % PMMA matrix. Concerning the PVC/PMMA blend, other investigations have shown that this system became immiscible beyond 60% weight of PMMA.^{8–11} However, Deshpande et al.¹² have shown by thermal studies that the blends cast from methylethylketone (MEK) were immiscible for 50 wt % of PVC. Wlochowicz et al.¹³ and Li et al.¹⁴ separately concluded by means of different techniques that the PVC/PMMA blends at all compositions were wholly amorphous two-phase systems and suggested that intermolecular forces between the two polymers were very weak. Two results from the literature are typical; Razinskaya et al.¹⁵ were unable to produce compatible blends of PMMA/PVC from tetrahydrofuran (THF). Walsh et al.¹⁶ have reportedly produced compatible blends using MEK as a common solvent. Schmitt et al.¹⁷ have also reported that blend cast from MEK has a higher degree of miscibility than the blends obtained from THF casting. Jager et al.¹⁸ have reported that atactic PMMA blended with PVC was miscible at all compositions when treated at 60°C. Melt blending at

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180°C, led to phase separation. Their conclusions are subtly different because of different blend preparations, the molecular weight of each constituent, and the tacticity of PMMA. The role of intermolecular interactions on the miscibility could be present in these blends.^{13,14,19} These types of intermolecular interactions have been considered as the hydrogen bonding interactions between the carbonyl group and the methyne proton, the dipole–dipole interaction between the carbonyl group and the carbon–chloride bond, and Lewis acid–base interaction between the carbonyl oxygen of an ester as an electron donor and the hydrogen of the CHCl groups as an electron acceptor. This type of other blends formed from PVC and copolymers have also been investigated by different authors.^{8,20} They have shown that the insertion of basic groups within the polymeric main chains as copolymers seemed to improve appreciably the miscibility of certain polymers.

Concerning the PVC/poly(butylmethacrylate)(PVC/PBMA) mixture, a further study has been carried out⁸ and it has shown that the insertion of 10–26 mol % of 4-vinylpyridine (4VP) groups in PBMA main chain improved the miscibility of the mixture. 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. The knowledge of the capability of PVC to develop the intermolecular interaction with other polymers is important because this fact allows forecasting the miscibility of blends involving the PVC.

As mentioned above, the miscibility of this system has been discussed widely but not completely elucidated. There are a few discussions of the miscibility based on thermodynamics for this system.

To improve the miscibility of PVC/PMMA system and the study capability of PVC to develop the intermolecular interaction with other polymers and their intensity, we have synthesized two copolymers of methylmethacrylate and vinylpyrrolidone (MMVP-10 and MMAVP-20) containing 8.23 and 14.71 wt % of vinylpyrrolidone (VP), respectively, through free radical polymerization and carried out a comparative study using inverse gas chromatography (IGC) and differential scanning calorimetry (DSC).

IGC has been used to determine different magnitudes of pure polymers and their blends. Among the others, glass transition temperature (T_g), the polymer–polymer interaction parameter ($\chi_{2,3}$),^{21–25} and the dispersive surface energy (γ_s^d)^{26,27} have been probably the main topics of the IGC studies. By the determination of $\chi_{2,3}$, IGC technique is adequate for proving the miscibility of pairs of polymers, especially for those polymers having the ΔT_g value between those of the pure constituents inferior to 20°C because the DSC method does not permit the

determination of T_g values accurately in this temperature range. In this investigation, for the first time attempted has been made to determine the polymer–polymer interactions parameters corrected ($\chi_{2,3}^{co}$) from the effect of solute.

EXPERIMENTAL

Materials

The solvents and the precipitants such as chloroform, THF, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane (Aldrich, 99% purity) were used without further purification.

Azo-bisobutyronitrile (AIBN) (Aldrich, 98% purity) was purified by recrystallization in methanol. The monomers, methylmethacrylate (MMA) and vinylpyrrolidone (VP) (Aldrich, 98% purity) were distilled under nitrogen atmosphere and kept at –20°C.

The PVC with *K* value 67 was supplied by SABIC, Kingdom of Saudi Arabia and purified by dissolution in THF and precipitated out with *n*-heptane.

The polymer blend PVC/MMVP was prepared in five mass ratios (10 : 90, 25 : 75, 50 : 50, 75 : 25, 90 : 10) by coprecipitation from THF solutions in excess of *n*-heptane. The blends were dried in a vacuum oven at 60°C for several days.

Polymerization and copolymerization

The copolymerization of MMA with VP has been carried out at 60°C for 90 min under nitrogen atmosphere, by free radical polymerization in THF using AIBN as initiator. The copolymers were purified by repeated dissolution in THF and precipitation in *n*-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 copolymerization conditions at different compositions. The molecular weights of MMVP-10 and MMVP-20 were estimated in THF at 30°C by size exclusion chromatography (SEC) on a Varian apparatus equipped with a JASCO HPLC-pump type 880-PU refractive index/UV detectors and TSK Gel columns calibrated with polystyrene standards. The compositions in comonomers VP in the copolymers have been determined by CHN analysis using Perkin–Elmer PE 2400 Series II apparatus. The results of characterization of PVC/MMVP-10 and PVC/MMVP-20 are also gathered in Table I.

Procedures and equipment

1. A gas chromatograph (GC-8A, Shimadzu) equipped with a dual flame ionization detector (FID) was used in this work. Chromosorb W was employed as a support (80 mesh, specific area of 1 m² g⁻¹). Before use, it was deactivated by

TABLE I
Synthesis and Characterization of MMVP-10 and MMVP-20 Copolymers

| Copolymer | AIBN (g) | Comonomer MMA (g) | Comonomer VP (g) | Yield (%) | Composition of VP in MMVP (wt %) | Composition of VP in MMVP (mol %) | \bar{M}_n |
|-----------|----------|----------------------|---------------------|-----------|-------------------------------------|--------------------------------------|-------------------|
| MMVP-10 | 0.02 | 4.5 | 0.5 | 12 | 9.06 | 8.23 | 4.2×10^5 |
| MMVP-20 | 0.02 | 4.0 | 1.0 | 10 | 16.35 | 14.71 | 7.4×10^5 |

acidic washing followed by treatment with dimethyldichlorosilane (DMCS).

2. Impregnation of the solid support: 0.20 g of polymer was dissolved in 20 mL of THF and the solution was placed into a 250 mL round-bottomed flask then 1.80 g of the support was added. The slurry (polymer and support) was well swirled before evaporation of the solvent to dryness by means of a rotary evaporator. The impregnated support by the polymer at this stage was further dried in a vacuum drying-oven at 60°C for 48 h. The dried solid was then sieved before packing in the columns. Seven columns containing different compositions in PVC/MMVP were prepared by this method and Table II shows the preparation conditions.
3. Packed columns were prepared from a 1-m long and 0.635 cm outer diameter stainless-steel tube. The tubes were first rinsed with acetone, after passing dry nitrogen gas through them, and dried under vacuum for 7 h at 60°C. Columns were thoroughly filled with the impregnated solid support. To ensure a homogeneous packing, the filling operation was secured with an electric vibrator. The loading was evaluated after calcinations realized during 1 h at 450°C following the Vogel method.²⁸ Characterization of the columns used in this work is given in Table II. Columns were conditioned at 110°C under a low carrier gas flow rate (3 mL min⁻¹) for 12 h before use.
4. Nitrogen was used as the carrier gas. Flow rate (10 mL min⁻¹), was measured with a soap-bubble flowmeter at room temperature. Three or more injections of an infinitesimal quantity, using a 1.0 μL Hamilton syringe, were carried

out for each probe. The net retention time was taken as the difference of the retention times of the probe and the methane peaks. The required thermodynamic data of solvents and polymers have been taken from the literature.^{29,30}

The glass transition temperature of the pure components and blends was measured with a DSC (Setaram Labsys DSC 16), previously calibrated with indium, at 20°C min⁻¹ rate. The samples of 10–15 mg were preheated to 200°C under nitrogen atmosphere to minimize the thermal degradation of the polymers and kept at that temperature for 10 min to ensure total elimination of solvent. The data were collected from the second scan. No degradation phenomenon of PVC and PVC/MMVP blends was observed in all thermograms. That was also confirmed by a test of solubility and NMR spectroscopy conducted after DSC analysis. The glass transition temperature was taken as the midpoint in the heat capacity change with temperature.

THEORY AND CALCULATION

IGC parameters

The specific retention volumes (V_g^o) were calculated from the expression²⁷:

$$V_g^o = \Delta t \frac{F}{w} \frac{3273.15 \left(\frac{P_i}{P_o}\right)^2 - 1}{Tr \left(\frac{P_i}{P_o}\right)^3 - 1}$$

where Δt is the net retention time (min); w the mass (g) of the polymer in the column, P_i and P_o the inlet

TABLE II
Stationary Phases and Columns Description

| Column composition (wt %) | PVC/MMVP-10 | | PVC/MMVP-20 | |
|------------------------------|-------------|-------------|-------------|-------------|
| | Support (g) | Polymer (g) | Support (g) | Polymer (g) |
| 100 : 0 | 1.689 | 0.173 | 1.689 | 0.173 |
| 90 : 10 | 1.413 | 0.161 | 1.766 | 0.196 |
| 75 : 25 | 1.560 | 0.177 | 1.722 | 0.160 |
| 50 : 50 | 1.555 | 0.178 | 1.533 | 0.199 |
| 25 : 75 | 1.455 | 0.168 | 1.636 | 0.187 |
| 10 : 90 | 1.427 | 0.170 | 1.632 | 0.178 |
| 0 : 100 | 1.547 | 0.169 | 1.695 | 0.194 |

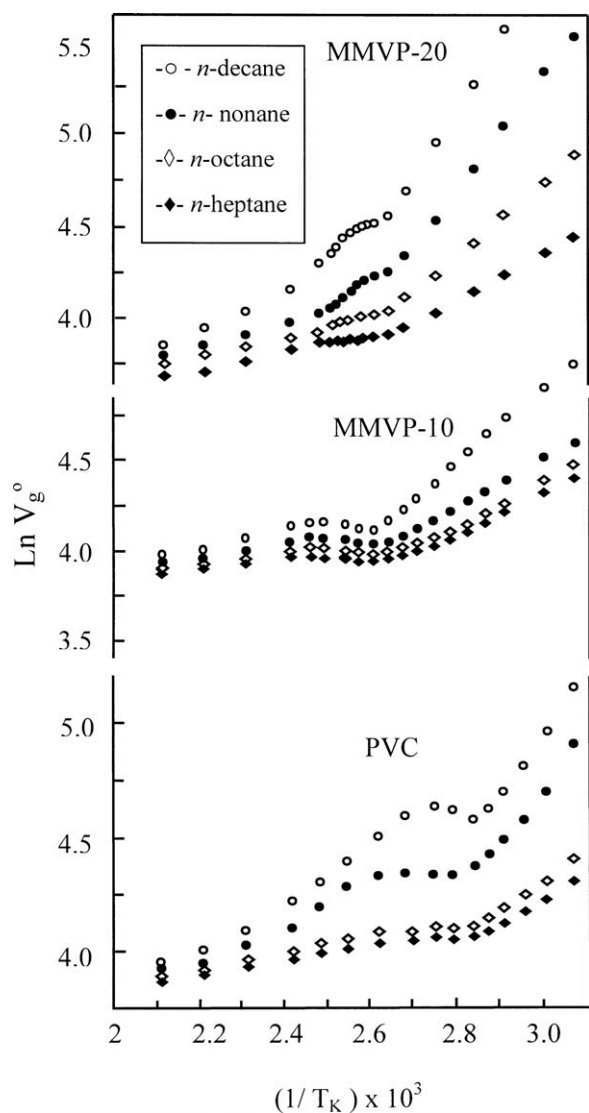


Figure 1 Retention diagrams of PVC, MMVP-10 and MMVP-20 using *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane as probes.

and outlet pressures (mmHg) and F is the carrier gas flow (mL min^{-1}) at room temperature, $T_r(\text{K})$. The values obtained for V_g^0 (mL) using the above given procedure were found to be good agreement within 5×10^{-3} mL for each measurement. Retention diagrams were generated by injecting seven probes (solutes) into the chromatographic columns, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane as a common non solvent for PVC, MMVP, and their mixtures in 50–200°C temperature range. The conditions of columns preparations are described in Table II. An additional column packed with only the solid support (0% blend) was used to obtain the contribution of support to the V_g^0 values as described earlier. Specific retention volumes (V_g^0) for the *n*-alkane solutes were calculated from the measured chromatographic quantities as described in eq. (1). The retention diagrams obtained at differ-

ent temperatures and different probes for PVC, MMVP-10, and MMVP-20 are shown in Figure 1 and those of PVC/MMVP-10 and PVC/MMVP-20 blends at 25, 50, and 75 wt % of PVC content are shown in Figures 2 and 3, respectively.

The shape of the retention diagram has been explained on the basis that, at the glassy state, the probe interacts with the polymer surface only due to the fact that the diffusion into the polymer is too slow to allow the bulk interaction.³¹ At the temperatures higher than T_g , the retention volume is a measure of the interaction of the probe with the bulk polymer in liquid state. Close to the T_g , both factors contribute to the retention volume, which increases with the solute penetrability. In relation to the straight-line regions, the negative slope is due to the increase of vapor pressure with temperature.^{32,33}

Flory-Huggins interaction parameters characterizing the interactions of the vapor-phase probe (1) with each of the two polymers (2) and (3) are determined from the retention data using three well-known equations^{34–36}:

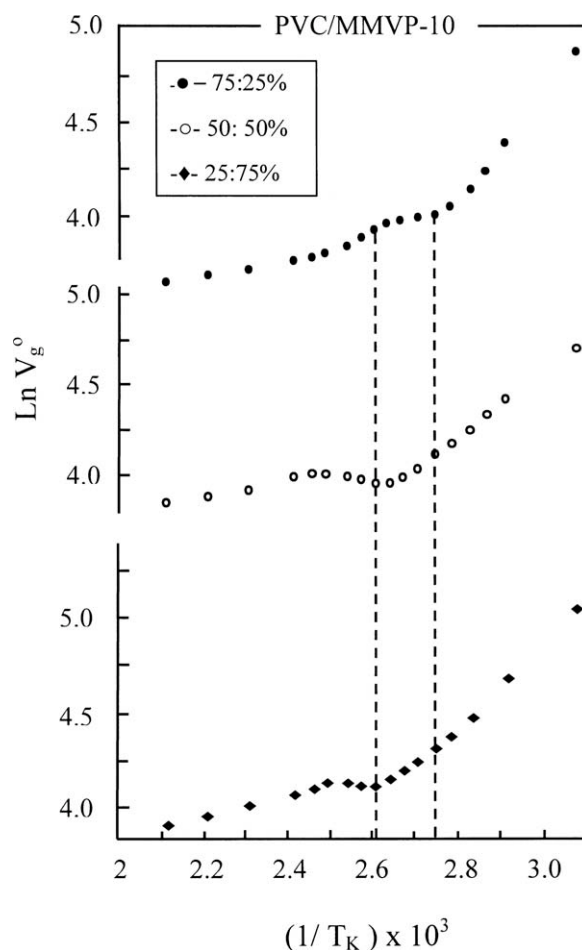


Figure 2 Retention diagrams of PVC/MMVP-10 (wt %) blends using *n*-decane as probes.

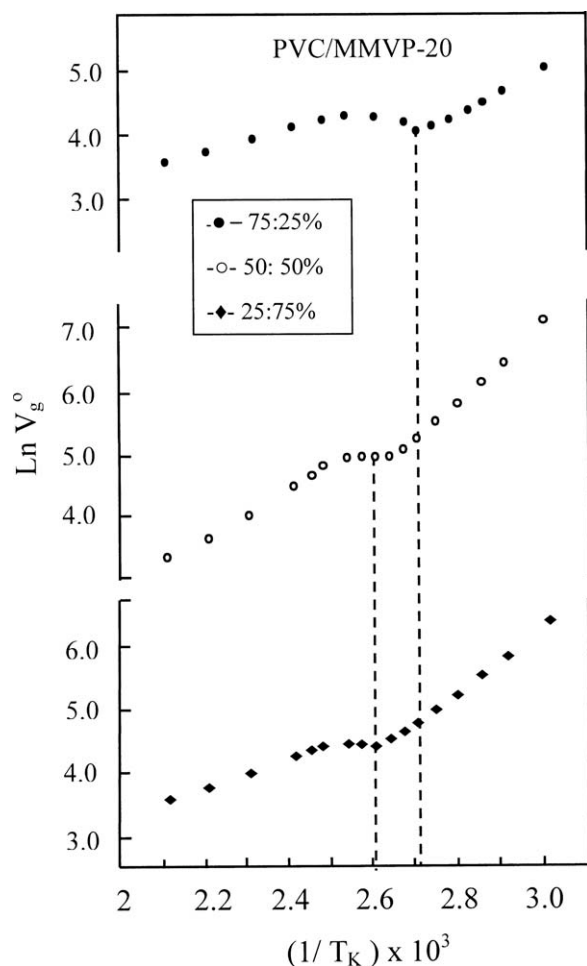


Figure 3 Retention diagrams of PVC/MMAVP-20 (wt %) blends using *n*-decane as probes.

$$\chi_{1,i} = \ln \left(\frac{273.15 \times R \times v_i}{V_{g,i}^o \times P_1^o \times V_1} \right) - \left(1 - \frac{V_1}{M_i \times v_i} \right) - \frac{P_1^o}{R \times T} (B_{11} - V_1)$$

The second term in the square brackets is reduced to unity for the high molecular weight stationary phases.^{34,37} The solute-polymer interaction parameter $\chi_{1,i}$ can be calculated from the V_g^o value using the following equation³⁸:

$$\chi_{1,i} = \ln \left[\frac{273.15 \times R \times v_i}{V_{g,1}^o \times V_1 \times P_1^o} \right] - 1 - \frac{(B_{11} - V_1)P_1^o}{R \times T}$$

where v_i is the specific volume of the polymer i and V_g^o is the specific retention volume of the solvent. V_i , P_1^o and B_{11} are the molar volume, vapor pressure, and second virial coefficient of the solute, respectively. When the stationary phase is a polymer blend, eq. (2) allows the determination of the ternary solute (1)–polymer (2)–polymer (3) interaction parameter, $\chi_{1(23)}$, assuming an additive specific vol-

ume for the polymer blend, $v_b = w_2v_2 + w_3v_3$ where w_i is the weight fraction of polymer i in the blend. On the contrary, assuming the Scott-Tompa approximation³⁹ which describes a ternary system as a simple balance of the corresponding binary systems in which the parameter $\chi_{1(23)}$ is affected by the interaction between the component polymers themselves, corresponding to χ_{23} ; it is possible to calculate the polymer–polymer interaction parameter, χ_{23} by:

$$\chi_{1(23)} = \chi_{12}\phi_2 + \chi_{13}\phi_3 - \chi_{23} \frac{V_1\phi_2\phi_3}{V_2}$$

where ϕ_i is the volume fraction of polymer i and V_2 the molar volume of polymer (2) at column temperature. In the framework of the Flory-Huggins theory, a reference volume must be defined to calculate the interaction parameter, thus, the polymer–polymer interaction parameter related to the solvent volume,²⁷

$$\chi'_{23} = \chi_{23} \frac{V_1}{V_2}$$

However, Al-Saigh and Munk³⁷ have demonstrated that if IGC measurements are carried out in identical experimental conditions of flow, temperature, inlet and outlet pressure, the polymer–polymer interaction parameter determination is greatly simplified. In these conditions, only the specific volumes and specific retention volumes of the pure polymers and the blends are required to obtain χ'_{23} values²⁷:

$$\chi'_{23} = \frac{\ln \frac{V_{g,b}^o}{v_b} - \phi_2 \ln \frac{V_{g,2}^o}{v_2} - \phi_3 \ln \frac{V_{g,3}^o}{v_3}}{\phi_2\phi_3}$$

As it has been mentioned above, the polymer–polymer interaction parameter determined by IGC shows a clear dependence on the solute used as a probe.

The required thermodynamic and physic data of solvents and polymer have been taken from usual compilations.^{37,40}

Surface energy of polymers

The surface energy (γ_s) describes the interactions due to dispersive forces or a combination of dispersive forces with hydrogen bonding, with dipole–dipole or acid–base forces. To determine the interaction of solute in the gaseous form with the polymer layer, the surface energy may be obtained from the Fowkes method.⁴¹ The contribution of dispersive forces can be expressed as the energy of adhesion as follows:

$$\gamma_a = \gamma^d + \gamma^{sp}$$

where γ^d is the contribution of dispersive forces and γ^{sp} is the contribution of specific interaction forces

such as hydrogen bonding, dipole–dipole, and acid–base. The IGC method was successfully applied in recent years to determine the surface properties of divided solids^{27,42–46} V_g^o relates to the equilibrium constant K between the absorbed solute and the polymer surface powder in the column (A) as follows:

$$V_g^o = K \times A$$

The molar free energy of adsorption (ΔG_s^a) of solute on the polymer layer may be defined in terms of the retention volume of the probes by the following equation:

$$\Delta G_{s1}^a = -RT \ln V_g^o + C$$

where T and C are the column temperature and a constant depending on A , respectively. Consequently, eq. (9) relates the energy of adhesion to the free energy of adsorption as follows:

$$RT \ln V_g^o = 2Na\sqrt{\gamma_s^d \gamma_i^d} + C$$

where γ_s^d and γ_i^d are the dispersive components of the solid surface and the interactive solutes phase, respectively. N is Avogadro's number and a is the area of the adsorbed molecules (solutes). If the n -alkane series is used, the results will represent the dispersive component of the surface energy (γ_s^d).

In IGC experiments, a series of interactive solutes, such as n -alkanes can be injected into the chromatographic column to determine the dispersive surface energy (γ_s^d). Thus, a plot of $RT \ln V_g^o$ versus the number of carbons of the n -alkane chain can be meaningful, because such a plot yields a straight line as showed in Figures 4 and 5 for the pure polymers (PVC, MMVP-10, MMVP-20) and their blends at 25 wt % PVC content (PVC/MMVP-10, PVC/MMVP-20) respectively, and their slopes yield ΔG_s^a . To accomplish such calculations, the molar free energy of adsorption of each CH_2 group in the n -alkane series ($\Delta G_a^{\text{CH}_2}$) may be calculated with precision. $\Delta G_a^{\text{CH}_2}$ value directly related to the square root of the product of γ_s^d and γ_i^d , the dispersive components of the solid surface and the interactive solutes phase, respectively. Therefore, the dispersive component of the surface energy (γ_s^d) can be readily calculated by the combination of eqs. (8) and (9) as follows

$$\gamma_s^d = \frac{1}{4\gamma_{\text{CH}_2}} \left(\frac{\Delta G_a^{\text{CH}_2}}{N \times a_{\text{CH}_2}} \right)^2$$

where γ_{CH_2} is the surface energy of a hydrocarbon consisting only of n -alkanes, a_{CH_2} is the area of one $-\text{CH}_2-$ group. Equation (10) usually tests the IGC

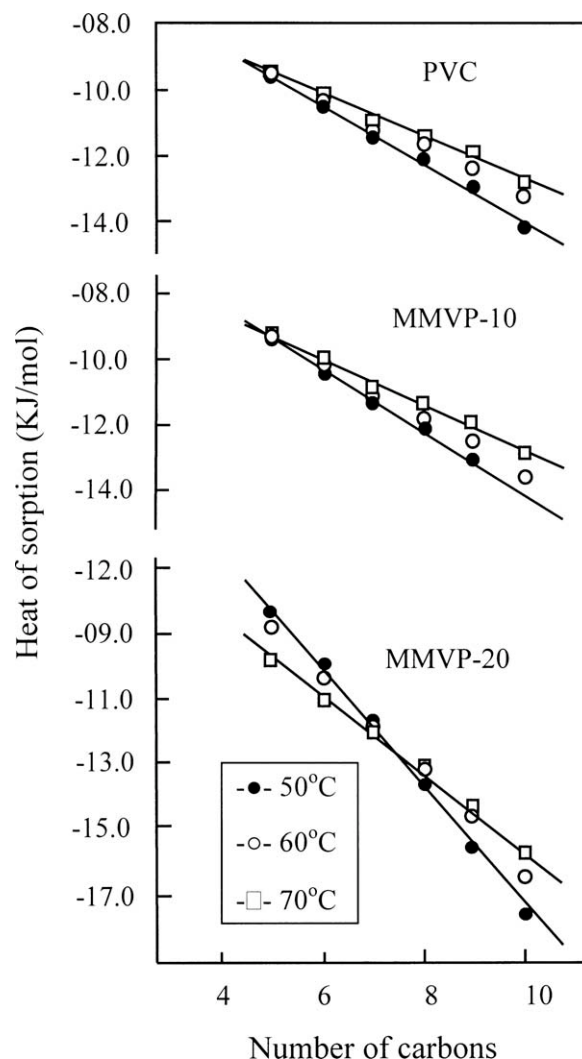


Figure 4 Family plot, the molar heat of sorption in KJ/mol of PVC, MMVP-10, and MMVP-20 versus the number of carbons in the solute (n -alkane).

method for obtaining the dispersive surface energy of polymers. The dispersive component of the surface energy could be calculated as a function of temperature from the eq. (10). According to several authors,^{47,48} the cross-sectional area of an adsorbed $-\text{CH}_2-$ group (a_{CH_2}) is estimated to be $6(A)^2$. The surface-free energy of a solid containing only $-\text{CH}_2-$ groups, γ_{CH_2} , is computed as a function of temperature as follows:

$$\gamma_{\text{CH}_2} = 36.80 - 0.058T$$

where T is the temperature in $^{\circ}\text{C}$.

DSC

To confirm the existence of intermolecular interactions between the constituents of the mixture, the Schneider approach⁴⁹ has been applied, this

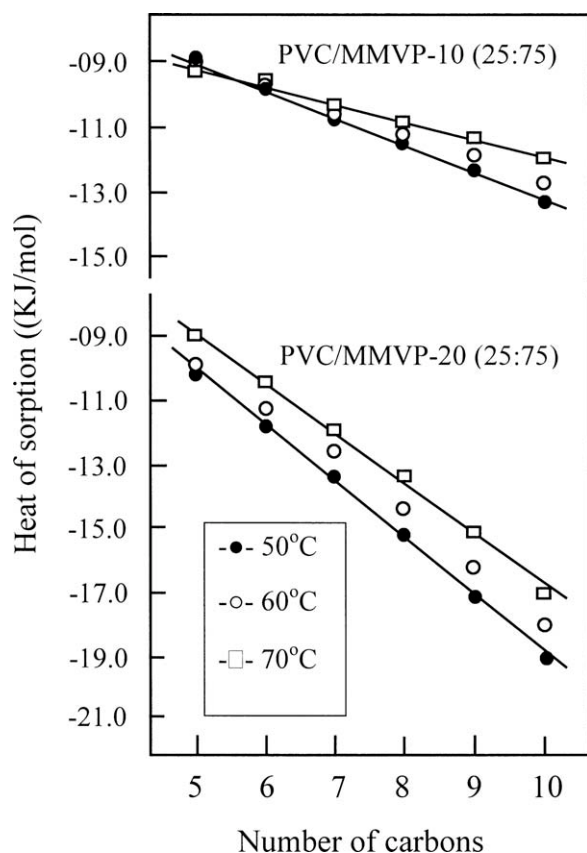


Figure 5 Family plot, the molar heat of sorption in KJ/mol of PVC/MMVP-10 and PVC/MMVP-20 blends at 25 wt % of PVC content versus the number of carbons in the solute (*n*-alkane).

relationship links the glass transition temperature of the blend, $T_g(m)$ with the glass transition temperature of the pure constituents $T_g(2)$ and $T_g(3)$ as follows:

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

where $W_{3C} = \frac{KW_3}{W_2 + KW_3}$ and $K = \frac{\rho_2 T_g^2}{\rho_3 T_g^3}$

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 the density of polymer (2) and polymer (3), respectively.

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

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

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 blend.

RESULTS AND DISCUSSION

Determination of glass transition temperature (T_g)

From IGC analysis, T_g has been measured as the temperature where the straight line obtained in the glassy state started to deviate from linearity, so, its slope has changed, as marked in Figures 1–3. This definition corresponded to the start detection of the glass transition event.⁴⁵ From the measurements carried out in this investigation, it was estimated that the error involved in the very start detection of the T_g by IGC was about 1°C. In Figure 1, the retention diagrams of *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane in MMVP-10 and MMVP-20 are shown. First, the probes allowed an adequate determination of T_g of these polymers but the transition region was more marked with the *n*-decane. Considering the retention diagrams of Figure 1 and similar diagrams obtained for PVC/MMVP-10 and PVC/MMVP-20 blends of Figures 2 and 3, respectively, it could be concluded that the molecular size of probe (*n*-alkane) is an important factor in determining the values of T_g accurately.

As can be seen in these chromatograms, only a single glass transition temperature was observed between those that characterized the pure constituents, indicating that these blends are miscible in all proportions. The glass transition temperatures deduced from these chromatograms and those obtained from the DSC thermograms of Figures 6 and 7 are gathered in Table III. The agreement between T_g data obtained by IGC was excellent and comparable with those determined by DSC methods. In a certain case, the small difference ($\sim 1^\circ\text{C}$) between T_g obtained by DSC and IGC was due to the effect of the solute, which played in this case the role of a plasticizer and led to mobility of the polymeric chains. Similar results were also observed by different authors^{19,23–25,27} who attributed this phenomenon to this same effect.

Determination of polymer–polymer interaction parameters ($\chi_{2,3}$)

In the liquid state, the IGC allows the determination of thermodynamic magnitudes,^{21–25} specially the interaction parameter that plays an important role as

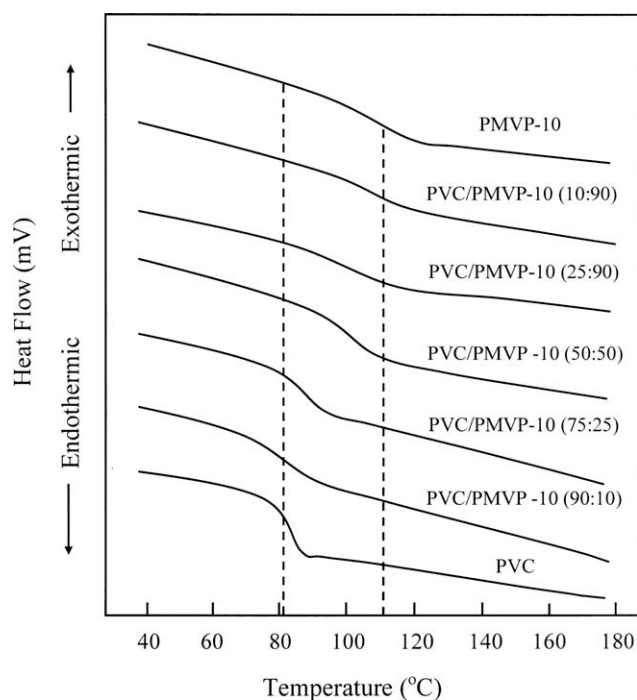


Figure 6 DSC thermograms of PVC/MMVP-10 blend at different compositions obtained at 20°C/min heating rate.

indicative of blend miscibility particularly in case where the components of the blend have similar T_g values, and consequently proving the miscibility of polymer blends from the comparison of T_g values become impossible.

The interaction parameters between PVC and MMVP have been calculated from eqs. (4) and (5) in 160–200°C temperature range using the specific volume of PVC at high temperatures obtained by dilatometry method from the literature.²⁹ Figures 8 and 9 show the polymer–polymer interaction parameters (χ_{23}) at different weight fractions of MMVP and different probes determined with average error

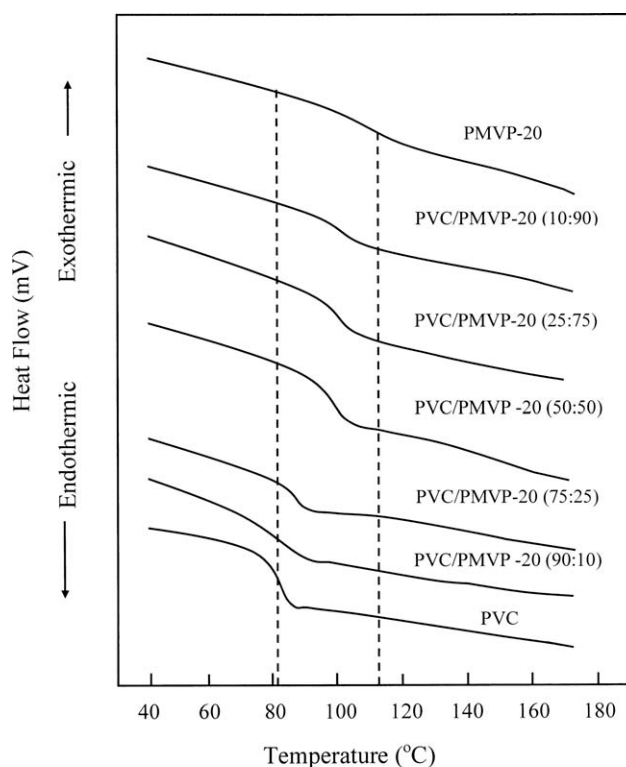


Figure 7 DSC thermograms of PVC/MMVP-20 blend at different compositions obtained at 20°C/min heating rate.

of ± 0.03 due to the experimental measurements of different parameters. For the two systems of different compositions, it has been observed from these Figures a perfect linearity of χ_{23} with the number of carbons probe. From this observation, it has been proven that, only the length of the *n*-alkane chains plays an important role in the retention dynamic. So, by a simple extrapolation of these straight lines to zero carbon (without solute), it has been possible to resolve the problem due to the influence of solute

TABLE III
Glass Transition Temperatures Determined by DSC and IGC Methods with $\Delta T_g = \pm 1^\circ\text{C}$

| System | T_g (DSC) (°C) | T_g (IGC) (°C) | | | |
|--------------------|------------------|-------------------|------------------|------------------|------------------|
| | | <i>n</i> -Heptane | <i>n</i> -Octane | <i>n</i> -Nonane | <i>n</i> -dEcane |
| PVC/MMVP-10 (wt %) | | | | | |
| 100 : 0 | 81 | – | – | – | – |
| 90 : 10 | 84 | 83 | 83 | 83 | 83 |
| 75 : 25 | 89 | 89 | 89 | 89 | 88 |
| 50 : 50 | 98 | 98 | 98 | 97 | 97 |
| 25 : 75 | 107 | 105 | 105 | 105 | 105 |
| 10 : 90 | 111 | 110 | 110 | 110 | 110 |
| 0 : 100 | 112 | 110 | 110 | 110 | 110 |
| PVC/MMVP-20 | | | | | |
| 90 : 10 | 84 | 83 | 83 | 83 | 83 |
| 75 : 25 | 87 | 86 | 86 | 86 | 86 |
| 50 : 50 | 97 | 96 | 96 | 96 | 96 |
| 25 : 75 | 100 | 99 | 99 | 98 | 98 |
| 10 : 90 | 104 | 103 | 103 | 103 | 102 |
| 0 : 100 | 108 | 107 | 107 | 107 | 107 |

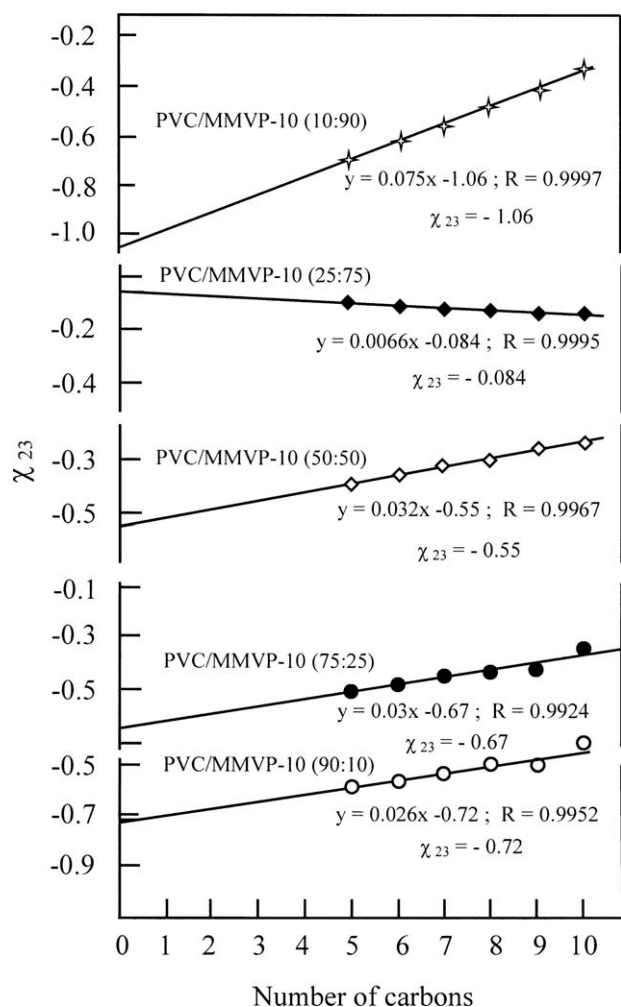


Figure 8 Interaction parameter, $\chi_{2,3}$, between PVC and MMVP-10 at different compositions (wt %) and at 160°C.

on the interaction parameter and consequently determine the corrected interaction parameters (χ_{23}^{CO}). Table IV illustrates the χ_{23}^{CO} of the PVC/MMVP-10 and PVC/MMVP-20 blends at different compositions and temperatures. According to the literature,²³⁻²⁵ the phase behavior has been corroborated by the polymer-polymer interaction parameter, χ_{23}^{CO} , which takes the negative values in case of the misci-

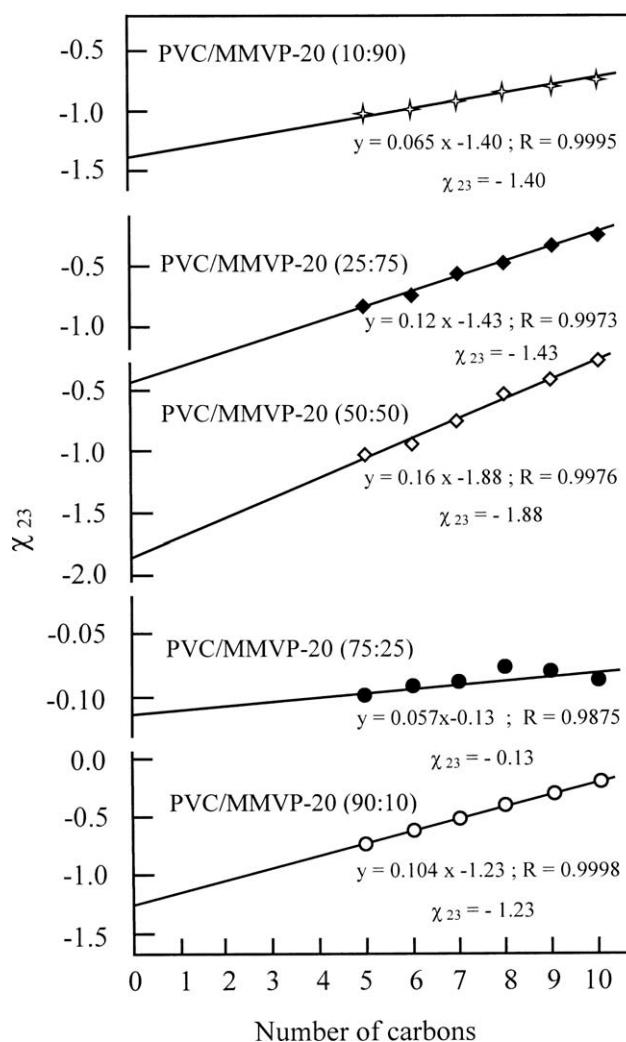


Figure 9 Interaction parameter, $\chi_{2,3}$, between PVC and MMVP-20 at different compositions (wt %) and at 160°C.

ble blends. From these data, a perfect miscibility of PVC/MMVP-10 and PVC/MMVP-20 systems in all compositions is appeared. These results indicate that, for PVC/MMVP-10 system, the interaction parameter varies with the composition between -0.084 ± 0.002 and -1.06 ± 0.03 and reach to a minimum at 25 wt % of MMVP-10 content while the

TABLE IV
The Corrected Interaction Parameter, $\chi_{2,3}^{CO}$, for PVC/MMVP-10 and PVC/MMVP-20 Blends at Different Compositions and Temperatures

| Blend composition (wt %) | $\chi_{2,3}^{CO}$ | | | | | |
|--------------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| | PVC/MMVP-10 | | | PVC/MMVP-20 | | |
| | 160°C | 180°C | 200°C | 160°C | 180°C | 200°C |
| 90 : 10 | -0.72 ± 0.02 | -0.92 ± 0.03 | -0.98 ± 0.03 | -1.23 ± 0.03 | -1.15 ± 0.03 | -1.28 ± 0.03 |
| 75 : 25 | -0.67 ± 0.02 | -0.63 ± 0.02 | -0.88 ± 0.02 | -0.057 ± 0.002 | -0.120 ± 0.003 | -0.131 ± 0.003 |
| 50 : 50 | -0.55 ± 0.02 | -0.302 ± 0.008 | -0.88 ± 0.02 | -1.88 ± 0.05 | -1.25 ± 0.03 | -1.25 ± 0.03 |
| 25 : 75 | -0.084 ± 0.002 | -0.053 ± 0.002 | -0.300 ± 0.008 | -1.43 ± 0.04 | -1.15 ± 0.03 | -1.28 ± 0.03 |
| 10 : 90 | -1.06 ± 0.03 | -0.96 ± 0.03 | -1.05 ± 0.03 | -1.40 ± 0.04 | -1.33 ± 0.04 | -1.30 ± 0.04 |

TABLE V
K Schneider Values for PVC/MMAVP-10 and PVC/
MMVP-20 Systems

| System PVC/MMVP-10 (wt %) | | System PVC/MMVP-20 (wt %) | |
|---------------------------------|--------------|---------------------------------|--------------|
| | K(Schneider) | | K(Schneider) |
| 90 : 10 | 1.36 ± 0.04 | 90 : 10 | 1.72 ± 0.05 |
| 75 : 25 | 1.38 ± 0.04 | 75 : 25 | 1.55 ± 0.04 |
| 50 : 50 | 1.34 ± 0.04 | 50 : 50 | 1.64 ± 0.05 |
| 25 : 75 | 1.24 ± 0.04 | 25 : 75 | 1.37 ± 0.04 |
| 10 : 90 | 1.12 ± 0.04 | 10 : 90 | 1.15 ± 0.03 |

PVC/MMVP-20 system shows a variation of χ_{23}^{CO} between -0.130 ± 0.004 and -1.88 ± 0.05 and reach to a minimum at 75 wt % of MMVP-20 content. In general, it has also been noted from these data that the interaction between PVC and MMVP-20 was higher than that of PVC and MMVP-10. This observation seems to be evident because the PVC/MMVP-20 blend contains more basic groups (vinylpyrrolidone) than PVC/MMVP-10 blend and consequently the intensity of interaction increases between the two polymers due to the presence of hydrogen bonding, dipole–dipole and acid–base interactions. From Table IV, In general, it has been observed in that the parameters (χ_{23}^{CO}) decreases weekly as the temperature increases.

Table V recapitulates the variation of the first term value of Schneider relationship $[T_g(m) - T_g(2)]/[T_g(3) - T_g(2)]$. W_{3c} obtained by DSC versus the corrected weight fraction W_{3c} of the two systems. These results have revealed a positive deviation compared with a horizontal straight line, an ordinate is equal to 1 and confirmed according to Schneider approach, due to the existence of interactions between the two polymeric constituents. These interactions reduced the free volume and mobility of the polymer chains and lead to rise in the T_g values.

Determination of surface energy

The surface energy of the pure polymers PVC, MMVP-10, MMVP-20 and their blends PVC/MMVP-

10 and PVC/MMVP-20 have been calculated from eq. (10) in a 50–70°C temperature range using the value of ΔG_a^{CH2} obtained from the slope of $RT \ln V_g^0$ versus the number of carbons of solute. Table VI shows the dispersive surface energy of MMVP-10 which ranged from $32.3 \pm 1.7 \text{ mJ m}^{-2}$ at 50°C to $17.1 \pm 0.9 \text{ mJ m}^{-2}$ at 70°C, while the surface energy of MMVP-20 showed higher values ($99.2 \pm 5.2 \text{ mJ m}^{-2}$ at 50°C to $46.4 \pm 2.4 \text{ mJ m}^{-2}$ at 70°C). The dispersive surface energy of PVC ranged from $36.8 \pm 1.9 \text{ mJ m}^{-2}$ at 50°C to $21.0 \pm 1.9 \text{ mJ m}^{-2}$ at 70°C, seemed to be in a good agreement with those of the literature,²⁶ while the γ_s^d of PVC/MMVP-10 and PVC/MMVP-20 blends showed a similar trend to that of their constituents, as they decreased with temperature. In general, the addition of MMVP-10 or MMVP-20 to PVC definitely should increase the dispersive surface energy of PVC and lower γ_s^d of MMVP-20. This is expected since MMVP was dispersed in PVC matrix and therefore solutes were probing the bulk of PVC by mixing process with the blend rather than adsorption process on the blend. The decrease in γ_s^d with the increase of temperature is expected since the surface of polymer expands as the temperature increases, thus allowing the microstructure start to be reorganized. Similar observations were reported on the poly(vinyl fluoride)/poly(vinylmethylketone) (PVF₂/PVMK) blend.²⁷

CONCLUSIONS

It can be concluded, from the results obtained in this investigation, that the IGC method is an appropriate technique to study the miscibility of PVC/MMVP blends through the glass transition temperatures and the interaction parameters. For both systems at different compositions, the miscibility has been approved and confirmed by DSC method through the presence of one T_g between those of the pure constituents attributed to the blend. From the data of the intermolecular interaction parameters determined by IGC

TABLE VI
Dispersive Surface Energies of Pure Polymers (PVC, MMVP-10, MMVP-20) and Blends (PVC/MMVP-10,
PVC/MMVP-20) at Different Compositions and Temperatures

| System composition (wt %) | $\gamma_s^d \text{ (mJ.m}^{-2}\text{)}$ | | | | | |
|------------------------------|---|------------|------------|--------------|-------------|-------------|
| | PVC/MMVP-10 | | | PVC/MMVP-20 | | |
| | 50°C | 60°C | 70°C | 50°C | 60°C | 70°C |
| 100 : 0 | 36.8 ± 1.9 | 32.0 ± 1.7 | 21.0 ± 1.1 | 36.8 ± 1.9 | 32.0 ± 1.7 | 21.0 ± 1.9 |
| 90 : 10 | 45.9 ± 2.4 | 10.3 ± 0.5 | 8.0 ± 0.4 | 131.1 ± 6.8 | 56.5 ± 2.9 | 66.0 ± 3.4 |
| 75 : 25 | 35.6 ± 1.9 | 16.6 ± 0.9 | 9.2 ± 0.5 | 35.6 ± 1.9 | 16.6 ± 0.9 | 10.8 ± 0.6 |
| 50 : 50 | 30.9 ± 1.6 | 47.4 ± 2.5 | 48.4 ± 2.5 | 218.7 ± 11.4 | 177.8 ± 9.2 | 112.5 ± 5.9 |
| 25 : 75 | 33.8 ± 1.8 | 12.2 ± 0.5 | 9.5 ± 0.5 | 102.7 ± 5.3 | 99.8 ± 5.2 | 148.2 ± 7.7 |
| 10 : 90 | 47.9 ± 2.5 | 16.6 ± 0.9 | 11.7 ± 0.5 | 138.14 ± 5.2 | 59.7 ± 3.1 | 73.9 ± 3.8 |
| 0 : 100 | 32.3 ± 1.7 | 22.9 ± 1.2 | 17.1 ± 0.9 | 99.2 ± 5.2 | 75.1 ± 3.9 | 46.4 ± 2.4 |

and DSC according to Schneider approach, it has suggested that the interactions between PVC and MMVP are moderately comparable with those that characterize the classical hydrogen bond and sometimes low, just barely enough to maintain a homogeneous polymer mixture away from phase separation. The influence of the solute (*n*-alkane) on the interaction parameters may be resolved by extrapolation to carbon zero of the straight line obtained from the variation of $\chi_{2,3}$ versus the number of carbons. The presence of interactions between PVC and MMVP confirmed the existence of different types of interaction: hydrogen bond (methylene proton of vinylchloride/carbonyl group of MMA; methylene proton of vinylchloride/nitrogen atom of VP); dipole-dipole (carbon-chloride bond/carbonyl group; carbon-chloride/nitrogen atom of VP); and Lewis acid-base (hydrogen of the CHCl groups an acceptor/carbonyl oxygen of an ester as electron donor; hydrogen of the CHCl groups as an acceptor/nitrogen atom of a tertiary amine as an electron donor).

The dispersive surface energy of PVC, MMVP-10, and MMVP-20 showed a similar trend to that of their blends, so they decreased with temperature. In general, the addition of MMVP to PVC increases the dispersive surface energy, which is an indication of the miscibility of these systems.

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