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Thermodynamic Study of Blends of Poly(4-vinylphenol-*co*-methyl methacrylate)/Poly(styrene-*co*-4-vinylpyridine) by Inverse Gas Chromatography

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Summary: Differential scanning calorimetry (DSC) and inverse gas chromatography (IGC) were used to determine the physicochemical properties of blends of poly(4-vinylphenol-co-methyl methacrylate) (PVPhMMA50) containing 50% of methyl methacrylate with poly(styrene-co-4-vinylpyridine) (PS4VPy 30) containing 30 mol% of 4-vinylpyridine. Specific retention volumes (V_g) and Flory-Huggins interaction parameter (χ_{1i}) for eight probes with different polarities were calculated at the 180–200 °C temperature range using PVPhMMA50, PS4VPy30 and their blends as stationary phases. Moreover, some thermodynamic properties of PVPhMMA50 and PS4VPy30 such as the weight fraction coefficient activity and the solubility parameters of both components (δ_2) were also calculated at infinite dilution. Both the obtained specific retention volume values with the different polymer blends and the calculated polymer-polymer interaction parameters (χ_{23}) allowed us to conclude that the binary blends of two polymers are miscible in all proportion. These results are in good agreement with the phase behaviour observed by DSC.

Keywords: blends; chromatography; miscibility; polymer-polymer interaction parameter (χ_{23}); poly(4-vinylphenol-co-methyl methacrylate)/poly(styrene-co-4-vinylpyridine)

Introduction

The research of new polymer materials with improved properties has become a subject of a large amount of academic work due to their very pertinent industrial applications. However, it has been established that in most cases polymer blends are immiscible due to their high molecular weight and the weak or the unfavorable interactions between the polymers.[1–3] In general, this fact is undesirable because, due to their poor mechanical properties, immiscible polymer blends are not used in a wide range of industrial applications.

For technological and theoretical considerations, the study of physicochemical properties of polymer materials is a very interesting area. Many experimental techniques have been used to determine the physicochemical parameters including calorimetry, melting point depression, sorption and small angle neutron scattering, etc. Unfortunately, most of these techniques are limited in their offering for several reasons. For example, it is extremely difficult to use the analytical techniques in order to measure thermodynamic properties of polymers due to their high melt viscosity. On the other hand, the direct methods available for the determination of the interaction between a polymer and non-polymeric compounds are few. However, over the five past decades, inverse gas chromatography has been successfully demonstrated as promising technique and effective tool to investigate the thermodynamic and surface properties of materials

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such as polymers, pharmaceutical products and organic pollutants.[4–6]

It has been established that inverse gas chromatography (IGC) can be used in order to determine many thermodynamic parameters, such as the activity coefficient, excess partial molar heats of mixing, solubility and polymer-solvent and polymer-polymer interaction parameters.[7] This technique is based on the traditional gas–solid/gas-liquid chromatography, but its goal is the characterization of the stationary phase instead of the separation of solutes in the mobile phase.

As it has been stated above, IGC has been largely applied to determine the polymer-polymer interaction parameter, χ_{23}. However, it has been shown that the nature of the solvent used as a probe has a large influence in the obtained χ_{23} value. This influence has been often ascribed to the so-called $\Delta\chi$ effect, related to the non-random partitioning of the probe. Attempts have been made from the perspective to resolve this dependency using several approaches.[8–10]

The present paper aimed to study the miscibility and the thermodynamic behaviour properties of poly(vinylphenol-co-methylmethacrylate) (PVPhMMA50), Poly(styrene-co-4-vinylpyridine)(PS4VPy30) and their blends using inverse gas chromatography, (IGC). Moreover, our interest here is particularly focused on looking for correlation between the observed phase behavior and the obtained thermodynamic parameters.

Experimental Part

Polymers and Characterizations

Poly(4-vinylphenol-co-methyl methacrylate) (PVPhMMA50) containing 50 mol% of MMA was purchased from Aldrich and used as received. The synthesis of PS4VP30 and methodology were described previously.[8]

The glass transition temperatures (Tg) 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.

Procedures and Equipment

The chromatographic support used in this study was Chromosorb W (acid washed and treated with dimethyldichlorosilane AW-DMSC) 80–100 mesh. Packed columns were prepared from a 150 cm 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 five hours at 60 °C. The two polymers were coated on the solid support by a soaking method.[9] Columns were conditioned at 190 °C under a fast carrier gas flow rate for 12 h prior to use. The total percent loading of polymer over the support, measured by calcination (1 h at 450 °C) was almost 7% in all cases. The characteristics of the columns are given in Table 1.

Measurements were carried out on a Varian gas chromatograph (model 3700) equipped with a flame ionization detector. Nitrogen was used as the carrier gas. Flow rate ($\approx$7 mL/min) 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

Table 1.
Polymer characteristics.

Column	Support (g)	Polymer (g)
PS4VP30	1.350	0.136
PVPhMMA50	1.467	0.147
PVPHMMA50/PSVP30 (4/1)	1.524	0.152
PVPHMMA50/PSVP30 (3/1)	1.470	0.147
PVPHMMA50/PSVP30 (2/1)	1.440	0.140
PVPHMMA50/PSVP30 (1/1)	1.535	0.154
PVPHMMA50/PSVP30 (1/2)	1.545	0.153
PVPHMMA50/PSVP30 (1/3)	1.484	0.148
PVPHMMA50/PSVP30 (1/4)	1.513	0.152

of solvents have been taken from usual compilations.[11]

Results and Discussion

DSC Study

Figure 1 displays the Tg vs composition representation corresponding to the PVPhMMA50/PSVPy30 blends. As it can be seen, the single glass transition temperature Tg observed in each blend, is an indication of their miscibility. The appearance of a single Tg suggests that the blends are completely homogenous. Furthermore, the Tg values of blends containing an excess of PVPhMMA50 are clearly higher than those calculated from the additive rule. A change in the shape of this curve is glimpsed with an increase of PVPhMMA50 in blend. Using the well known Kwei equation and from the positive value of the Kwei constant ($q = 67$), the Tg-composition analysis reveals the presence of strong specific interactions occurring between unlike species in the blend. The maximum of specific interactions may be found approximately at a ratio of 3/1 PVPhMMA50/PS4VPy 30. This trend could be due the formation of the strong intermolecular interactions between hydroxyl groups of vinylphenol (VPh) and nitrogen atoms of vinylpyridine (VPy), where these blends are able to form interpolymer complexes.

Inverse Gas Chromatography Study

Experimental specific retention volume

In order to analyse the miscibility of PVPhMMA50/PSVPy30, the specific retention volumes of the corresponding copolymers and their blends were measured in the temperature range 180–200 °C when the thermodynamic equilibrium was achieved. As can be seen in Figure 2, the plot of experimental specific retention volumes of the blend as function of PVPhMMA 50 weight fraction in all the checked probes, gives a concave curve, thus, a negative deviation from the additive rule is clearly observed.

This behaviour might be due to the unfavourable ability of the probes to interact with the stationary phase, which is reflected by their less retention in the column. Actually, this evolution could be considered as an evidence of the miscibility of these blends. In this case, the thermodynamic magnitudes between polymer (2) and polymer (3) in the blend are more predominant than those predicted using the additive rule of solute-polymer (2) and solute-polymer (3) data. From this fact, it could be interpreted that strong interactions occurred between the hydroxyl groups of PVPhMMA50 and the nitrogen atom of PSVPy30 in the blend. The maximum of these interactions was observed again with blend PVPHMMA50/PSVPy30 in the ratio (3/1).

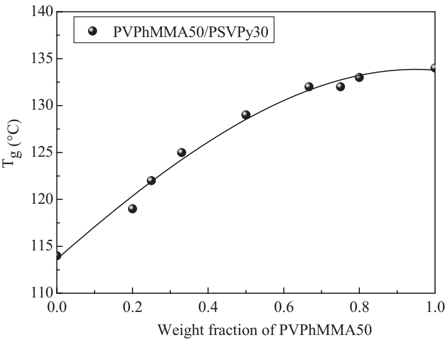

Figure 1.
Tg-Composition versus weight fraction of PVPhMMA50 in blend.

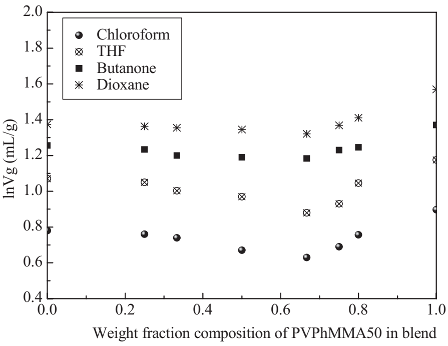

Figure 2.
Evolution of specific retention volumes (V_g) of blend PVPhMMA50/PSVPy30 versus PVPhMMA50 weight fraction at 180 °C.

Table 2.
True polymer-polymer interaction parameter (χ_{23}) and determined correlations.

Weight fraction of PVPhMMA50 in blend	(χ_{23}/v) 10^3 (mol/cm^3)	R^2
0.20	−1.00	0.998
0.25	−1.25	0.996
0.33	−1.45	0.997
0.50	−2.00	0.994
0.67	−2.35	0.997
0.75	−2.42	0.993
0.80	−1.95	0.996

True polymer-polymer interaction parameter

In order to quantify the intensity of these interactions that might be occurring in the blends of PVPhMMA50 and PSVPy30, we have calculated the true polymer-polymer interaction parameter (χ_{23}) using only experimentally measured magnitudes such as specific volumes (v) and specific retention volumes (V_g), we preferred to utilize the rearranged equation that can be expressed by:[12]

$$\left[\frac{1}{V_1}\ln\left(\frac{V^0_{g,b}}{v_b}\right)\right] = \left[\frac{1}{V_1}\left(\phi_2\ln\left(\frac{V^0_{g,2}}{v_2}\right) + \phi_3\ln\left(\frac{V^0_{g,3}}{v_3}\right)\right)\right] + \frac{\chi_{23}}{V_2}\phi_2\phi_3 \tag{1}$$

Therefore, a plot of the left side term as a function of the expression between brackets of the right side term of this equation allows us to calculate the true polymer-polymer interaction parameter from the intercept. Table (II) summarizes the polymer-polymer interaction parameters for five different compositions of PVPhMMA50/PSVPy30. As it can be seen, the negative values of (χ_{23}) are indicative that the different blends are completely miscible.

Conclusion

In this work, the miscibility of PVPhMMA50 with PS4VPy30 has been investigated by DSC and IGC. This miscibility was firstly evidenced by DSC where a single Tg was detected for each composition of the blends. The positive deviation of Tg values from average of the glass transition of pure components reveal that this miscibility may be due to the presence of specific interactions occurring between the two polymers. IGC results also confirm this miscibility qualitatively taking account the negative deviation of the obtained specific retention volumes of the blends with those calculated using the additive rule of pure component data. Moreover, this qualitative interpretation has been corroborated quantitatively by means of negative values for the true polymer-polymer interaction parameter (χ_{23}).

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