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Inverse Gas Chromatography in Characterization of Composites Interaction

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1. Introduction

Inverse gas chromatography is a useful and quite versatile technique for materials' characterization, because it can provide information on thermodynamic properties over a wide temperature range. The term "inverse" indicates that the stationary phase of the chromatographic column is of interest, in contrast to conventional gas chromatography. The chromatographic column contains the material under study. The method is simple, fast and efficient. It has been used for the characterization of hyperbranched polymers [Dritsas et al., 2008], block copolymers [Zou et al., 2006], polymer blends [Al-Ghamdi & Al-Saigh, 2000], nanocomposites [Boukerma et al., 2006], fillers [Milczewska & Voelkel, 2002], cement pastes [Oliva et al., 2002], fibers [van Asten et al., 2000] and crude oils [Mutelet et al., 2002].

Mixtures of different types of materials i.e. polymers, blends, modified fillers or compositions are utilized extensively to produce commercially useful materials having combinations of properties not revealed by a single component. Many of the properties and processing characteristics of those mixtures depend on whether they are miscible or not. Theory operates with parameters relating to the pure components [Voelkel et al., 2009 (a)]. The knowledge of the interaction parameters between polymers and solvents is very important in the study of their miscibility and thermodynamic properties of solutions [Huang, 2009].

The interactions between one probe and the polymer are usually characterized by the values of Flory–Huggins interaction parameter [Dritsas et al., 2009]. Only a few techniques can provide quantitative information about the change of free energy when mixing two components. The data from P-V-T experiments might be successfully used in the prediction of the miscibility of polyolefine blends [Han et al., 1999]. Interaction parameter for the components of polymer blends was also determined with the use of small angle x-ray scattering (SAXS) [de Gennes, 1979; Meoer & Strobl, 1987; Ying et al. 1993], thermal induced phase separation (TIPS) [Sun et al., 1999] and small angle neutron scattering (SANS) [Fernandez et al., 1995; Hindawi et al., 1990; Horst & Wolf, 1992; Mani et al., 1992; Schwann et al., 1996]. In last two decades, the Flory-Huggins interaction parameter was also

determined using the melting point depression method for crystal-containing polymers by differential scanning calorimetry (DSC) [Lee et al., 1997]. It is worth to note the increasing role of inverse gas chromatography (IGC) [Voelkel et al., 2009 (a)], because of its simplicity, rapidity, and the general availability of GC equipment.

2. Theory of interaction

Inverse Gas Chromatography (IGC) is a gas-phase technique for characterizing surface and bulk properties of solid materials. The principles of IGC are very simple, being the reverse of a conventional gas chromatographic (GC) experiment.

While it is a dynamic method, it was shown many years ago that measurements recorded under the correct conditions could give accurate equilibrium thermodynamic information [Shillcock & Price, 2003]. The retention of a solvent or 'probe' molecule on the material is recorded and the measurement made effectively at infinite dilution of the probe. A range of thermodynamic parameters can then be calculated. One advantage of the method is that it is readily applied to mixtures of two or more polymers.

A cylindrical column is uniformly packed with the solid material of interest, typically a powder, fiber or film. A pulse or constant concentration of gas is then injected down the column at a fixed carrier gas flow rate, and the time taken for the pulse or concentration front to elute down the column is measured by a detector. A series of IGC measurements with different gas phase probe molecules then allows access to a wide range of physico-chemical properties of the solid sample [SMS-iGC brochure 2002].
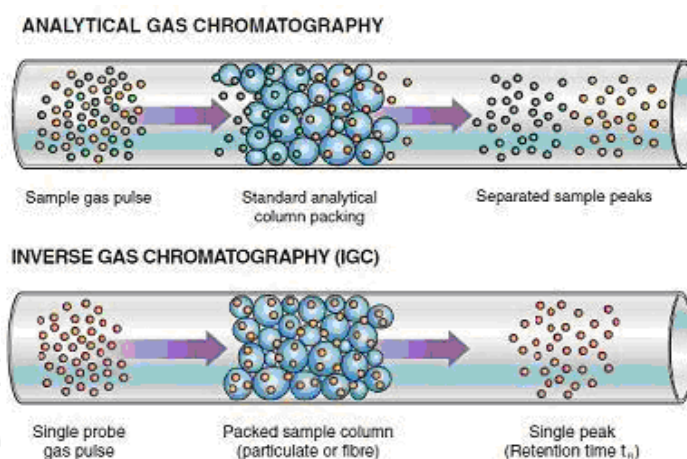

Fig. 1. Analytical vs. Inverse gas chromatography

When a liquid probe is injected into the column, the probe vaporizes and flows with the carrier gas, and a characteristic specific retention volume (V_g) can be measured:

$$V_g = \frac{3}{2} \cdot \frac{t_R' \cdot j \cdot F \cdot 273.15}{m_w \cdot T} \tag{1}$$

where: $t_R' = t_R - t_M$, t_M - gas hold-up time, calculated by Grobler–Balizs procedure [Grobler & Balizs, 1974], j – James-Martin's coefficient [James & Martin, 1952].

3. Flory-Huggins parameters

The properties of polymer blends are determined mainly by the miscibility of the components and structure. Usually thermodynamic miscibility and homogeneity can be attained when the free energy of mixing is negative. The classical thermodynamics of binary polymer–solvent systems was developed independently by P.J. Flory [Flory, 1942] and M.L. Huggins [Huggins, 1942]. It is based on the well-known lattice model qualitatively formulated by K.H. Meyer [Meyer, 1939], who pointed out the effect of the differences in molecular size of polymer and solvent molecules on the entropy of mixing. The quantitative calculation of the entropy of mixing led to the introduction of a dimensionless value, the so-called Flory-Huggins interaction parameter, for the thermodynamic description of polymer solutions [Gundert & Wolf, 1989]. Flory–Huggins interaction parameter (χ) is an important factor of miscibility of polymer blends and solutions.

Using Flory–Huggins theory, the Flory–Huggins interaction parameter between a polymer and probe, χ, can be related to the specific retention volume of probes, V_g, by the following equation [Milczewska & Voelkel, 2002 as cited in Barrales-Rienda, 1988; Voelkel et al., 2009 (b) as cited in Voelkel & Fall, 1995]:

$$\chi_{12}^{\infty} = \ln\left(\frac{273.15 \cdot R}{p_1^o \cdot V_g \cdot M_1}\right) - \frac{p_1^o}{R \cdot T} \cdot \left(B_{11} - V_1^o\right) + \ln\left(\frac{\rho_1}{\rho_2}\right) - \left(1 - \frac{V_1^o}{V_2^o}\right) \tag{2}$$

1 denotes the solute and 2 denotes examined material, M_1 is the molecular weight of the solute, p_1^o is the saturated vapor pressure of the solute, B_{11} is the second virial coefficient of the solute, V_i^o is the molar volume, ρ_i is the density, R is the gas constant.

This equation may be rearranged into form including weight fraction activity coefficient:

$$\ln \Omega_1^{\infty} = \ln\left(\frac{a_1}{w_1}\right) = \ln\left(\frac{273.15 \cdot R}{p_1^o \cdot V_g \cdot M_1}\right) - \frac{p_1^o}{R \cdot T} \cdot \left(B_{11} - V_1^o\right) \tag{3}$$

$$\chi_{12}^{\infty} = \ln \Omega_1^{\infty} + \ln\left(\frac{\rho_1}{\rho_2}\right) - \left(1 - \frac{V_1^o}{V_2^o}\right) \tag{4}$$

When the data of the density and the molecular mass of both the solute and the stationary phase (polymer) are inaccessible it is possible to determine the Flory-Huggins interaction parameter by simplifying Eq. (4):

$$\chi_{12}^{\infty} = \ln \Omega_1^{\infty} - 1 \tag{5}$$

i.e., under the assumption that $\ln\left(\frac{\rho_1}{\rho_2}\right) = 0$ which means that the densities of the solute and

the stationary phase are of similar order and $\frac{V_1^o}{V_2^o} \to 0$ (the molar volume of the stationary

phase is much higher than that of the test solute) [Voelkel & Fall, 1997].

Etxabarren et al. [Etxabarren et al., 2002] described molecular mass, temperature and concentration dependences of the polymer-solvent interaction parameter. The concentration dependence has been reasonably explained after the consideration of the different compressibilities (or free volumes) of the components. A parabolic dependence of χ with temperature is necessary in order to explain the lower or upper critical solution temperatures characteristic of most of the polymer solutions. In fact, there are experimental evidences of such type of dependence although because of limitations imposed by the degradation of the polymer and the freezing point of the solvent, a limited temperature range can be studied and only a part of this parabolic curve is usually evidenced.

Molecular mass dependence of the interaction parameter has been a recurrent subject in the polymer literature, and Petri et al. [Petri et al., 1995] have reported new experimental results which seem to indicate that there is a real molecular mass dependence of χ, especially in the range of moderate concentrations [Schuld & Wolf, 2001].

Ovejero et al. [Ovejero et al., 2009] determined Flory-Huggins parameter χ_{12}^{∞} for SEBS triblock copolymer. They noticed that Flory-Huggins parameter was defined as independent of concentration, but the effect of concentration is not negligible. Authors tried to develop a thermodynamic tool to simulate a polymer - solvent separation. In their work they also paid attention to temperature dependence. A decrease of Flory-Huggins parameter while increasing temperature was suggested. However they have shown that this dependence is not clear. For investigated rubber values of χ_{12}^{∞} increased slightly with temperature.

When mixture of components is used as a stationary phase in a chromatographic column, subscripts 2 and 3 are used to represent first and second mixtures' component, respectively [Voelkel et al., 2009 (b)]:

$$\chi_{1m}^{\infty} = \ln\left(\frac{273.15 \cdot R}{p_1^o \cdot V_g \cdot M_1}\right) - \frac{p_1^o}{R * T} \cdot \left(B_{11} - V_1^o\right) + \ln\left(\frac{\rho_1}{\rho_m}\right) - \left(1 - \frac{V_1^o}{V_2^o}\right) \cdot \varphi_2 - \left(1 - \frac{V_1^o}{V_3^o}\right) \cdot \varphi_3 \qquad (6)$$

where φ_2 and φ_3 are the volume fractions of components.

When $\chi < 0.5$, the probe liquid is generally characterized as a good solvent for the polymer, whereas $\chi > 0.5$ indicates a poor solvent which use may lead to phase separation. In the case of a polymer blend, the parameter χ can still be defined and the miscibility generally occurs when $\chi < 0$, because the high molar volume of both components diminishes the combinatorial entropy [Huang, 2009].

When a polymer blend is used the interaction between the two polymers is expressed in terms of χ_{23}' as an indicator of the miscibility of the components of the polymer blend. If the parameters χ_{12}^{∞} and χ_{13}^{∞} are known (from IGC experiment with appropriate component "2" or "3") the interaction parameter χ_{23}' may be calculated from equation [El-Hibri et al., 1989; Olabisi, 1975]:

$$\chi_{23}' = \frac{1}{\varphi_2 \cdot \varphi_3} \cdot \left(\chi_{12}^{\infty} \cdot \varphi_2 + \chi_{13}^{\infty} \cdot \varphi_3 - \chi_{1m}^{\infty}\right) \qquad (7)$$

Here, the second subscript of χ identifies the nature of the column.

The interaction between the two components of composition is expressed in terms of χ'_{23} may be also calculated from [Milczewska et al., 2001 as cited in Li (Pun Choi), 1996, Milczewska et al., 2003 as cited in Voelkel & Fall, 1997]:

$$\chi'_{23} = \frac{\chi^\infty_{23} \cdot V_1}{V_2} = \frac{1}{\varphi_2 \cdot \varphi_3} \cdot \left(\ln \frac{V_{g,m}}{W_2 \cdot v_2 + W_3 \cdot v_3} - \varphi_2 \cdot \ln \frac{V_{g,2}}{v_2} - \varphi_3 \cdot \ln \frac{V_{g,3}}{v_3} \right) \quad (8)$$

Here, the second subscript of V_g identifies the nature of the column. From Eq. (8), χ'_{23} may be calculated even for probes for which the parameters p^o_1, B$_{11}$ and V^o_i are not known or are known with insufficient accuracy [Al-Saigh & Munk, 1984].

To obtain χ'_{23} for a polymer blend or composition utilizing IGC, χ^∞_{12} values for all components have to be known. Therefore, three columns are usually prepared: two for single components and the third one for a composition of the two components used. A further three columns containing different compositions of components can also be prepared if the effect of the weight fraction of the mixture on the examined property needs to be explored. These columns should be studied under identical conditions of column temperature, carrier gas flow rate, inlet pressure of the carrier gas, and with the same test solutes [Al-Saigh, 1997].

Large positive values of χ'_{23} indicates the absence or negligible interactions between components, a low value indicates favorable interactions, while negative value indicates strong interactions (the pair of polymers is miscible).

Equations (7) or (8) were frequently used to study the interaction parameter between two stationary phases using the IGC method. In literature data, it was found that, in many miscible systems, χ'_{23} values were probe dependent. The values of χ'_{23} were positive when χ^∞_{12} and χ^∞_{13} were positive, and decreased when χ^∞_{12} and χ^∞_{13} decreased to negative. Some negative χ'_{23} values were generally observed for probes with low χ^∞_{12} and χ^∞_{13} [Huang, 2009].

Nesterov and Lipatov [Nesterov & Lipatov, 1999] studied thermodynamics of interactions in the ternary system: polymer A + polymer B + filler S. In their studies it was shown that the introduction of a third component into the binary immiscible mixture of two polymers, where the third component is miscible with each component of binary mixture, may lead full miscibility of the ternary system. For the immiscible mixtures of polyolefins with polyacrylates and polymethacrylates it was discovered that a mineral filler (e.g. silica) also may serve as compatibilizer.

The compatibilization effect of two immiscible polymers by adding the third polymer (or filler) my be described in the framework of the Flory-Huggins theory extended for describing ternary mixtures. For that mixtures Flory-Huggins parameter can be expressed as:

$$\chi_{A+B+C} \cong \chi_{AB} \cdot \varphi_A \cdot \varphi_B + \chi_{AC} \cdot \varphi_A \cdot \varphi_C + \chi_{BC} \cdot \varphi_B \cdot \varphi_C \tag{9}$$

A positive value of the parameter χ_{A+B+C} corresponds to an immiscible systems whereas a negative is an indicator of miscibility [Nesterov & Lipatov, 2001].

Values of Flory-Huggins χ'_{23} parameter depend on chemical structure of the solute and it is a common phenomenon, although not allowed by the theory [Fernandez-Sanchez et al., 1988]. It has been interpreted as a result of preferential interactions of the test solute with one of two components. This phenomenon for polymer blends was described independently by Fernandez-Sanchez et al. and Olabisi [Olabisi, 1975]. They attributed this to the non-random distribution of the solute in the stationary phase owing to its preferential affinity for one of the components. Selective solutes do not "sense" the three varieties of intramolecular contacts in the polymer mixture (A-A, A-B, B-B) in proportion to concentration. This modifies the retention volume (and χ'_{23}) values relative to those which would be obtained by truly random mixing of the solute with the polymer. Less selective solvents, on the other hand, exhibit a more random 'sampling' of the molecular environment of the stationary phase owing to the equal affinities they have for both. It is therefore expected that a better measure of the polymer-polymer interaction will be likely with less selective solvents.

Olabisi [Olabisi, 1975] described a polyblend as micro heterogeneous, where the size of the different phases and their interpenetration being limited by a host of factors among which are the extents of mixing, compatibility, molecular weight, clustering behaviour of each polymer, rheological and surface and interfacial properties. He attributed Flory-Huggins parameter dependence on test solute to unequal distribution of the solute in the stationary phase, and to wide range of interactions (polar, nonpolar, hydrogen-bonding and also electronic and electrostatic interactions) [Li, 1996]. Olabisi proposed to use a set of solvents based on their type of interactions with probe: (i) proton accepting strength, probed with chloroform and ethanol; (ii) proton donor strength with methyl-ethyl ketone and pyridine; (iii) polar strength with acetonitrile and fluorobenzene; (iv) nonpolar strength with hexane and carbon tetrachloride.

Prolongo et al. proposed to calculate the polymer-polymer interaction parameter χ from measurements performed on ternary systems composed of the polymer pair plus a solvent or probe. They given the expressions needed to calculate the true polymer-polymer χ based on the equation-of-state theory and they compared that method for PS+PVME data obtained from vapor sorption (VP). The results show that the values obtained from IGC correlation and VP are nearly the same [Prolongo et al., 1989].

Many authors suggest that the χ'_{23} values are solvent (solute) independent for probes giving $\chi^{\infty}_{12} = \chi^{\infty}_{13}$ [Su & Patterson, 1977; Lezcano et al., 1995]. If the difference between the interaction of the components (for blend ≡ polymers 2 and 3) with the solvent is negligible $\left| \chi^{\infty}_{12} - \chi^{\infty}_{13} \right| = \Delta\chi \approx 0$ interaction parameter χ'_{23} should be solvent independent. The equation above is often called "Δχ effect".

Horta's group [Prolongo et al., 1989] have proposed a method based on the equation-of-state theory, which gives a polymer-polymer parameter χ_{23} named 'true', because the

assumption that the Gibbs mixing function for the ternary polymer-polymer-solvent system is additive with respect to the binary contributions is avoided. They suggested that it is necessary to substitute the volume fraction φ_i in the Flory-Huggins theory by segment fractions ϕ_i according to:

$$\phi_i = \frac{w_i \cdot v_i^*}{\sum w_i \cdot v_i^*} \tag{10}$$

where v_i^* and w_i represent characteristic specific volume and the weight fraction of the ith component, respectively.

Shi and Shreiber [Shi & Shreiber, 1991] stated that the probe dependence of χ_{23}' is due to two major contributing factors. Firstly, the surface composition of a mixed stationary phase will rarely, if ever, correspond to the composition of the bulk. Thermodynamic requirements to minimize the surface free energy of the stationary phase will favor the preferential concentration, at the surface, of the component with the lower (lowest) surface free energy. Thus, the values of φ_2 and φ_3, as defined by the bulk composition of mixtures, are inapplicable to Eq. (7). Instead, a graphical method was proposed by Shi and Schreiber to evaluate the effective volume fraction and to correct the problem. Secondly, since χ_{12}^∞ and χ_{13}^∞ will not usually be equal, it follows that the volatile phase will partition preferentially to the component that has the lower pertinent χ_{1m}^∞ value. Thus, the partitioning must vary with each probe, inevitably affecting the χ_{23}' datum.

Deshpande and Farooque were the first to suggest the use of IGC for studying polymer blends [Deshpandee et al., 1974]. Starting form the Flory-Huggins expression for the change of the free enthalpy in mixing, which was extended to three-component systems, they proposed a method of analysis of IGC measurements on polymer blends which yielded the polymer-polymer interaction parameter χ_{23}'. They also observed probe dependency and tried to develop a method to evaluate probe-independent interaction [Farooque et al., 1992].

Milczewska and Voelkel [Milczewska & Voelkel, 2006] mentioned some of that methods of evaluating probe-independent interaction parameter. One of the solution may be procedure proposed by Zhao and Choi [Zhao & Choi, 2001; Zhao & Choi, 2002]. Authors proposed to use 'common reference volume' which vanishes the problem. As the reference volume they used molar volume of the smallest repeated unit of polymer.

Flory-Huggins parameter for blends can be calculated from equations:

$$\chi_{1m} = \frac{V_o}{V_1} \cdot \left(\ln \frac{273.15 \cdot R}{M_1 \cdot V_g \cdot p_1^o} - 1 + \left(1 - \frac{V_1}{V_2}\right) \cdot \varphi_2 + \left(1 - \frac{V_1}{V_3}\right) \cdot \varphi_3 - \left(\frac{B_{11} - V_1}{R \cdot T}\right) \cdot p_1^o \right) \tag{11}$$

and

$$\chi_{1m} = \varphi_2 \cdot \chi_{12} + \varphi_3 \cdot \chi_{13} - \varphi_2 \cdot \varphi_3 \cdot \chi_{23}' \tag{12}$$

Equation (12) predicts that a plot of χ_{1m} versus $(\varphi_2 \cdot \chi_{12} + \varphi_3 \cdot \chi_{13})$ will give a straight line with a slope 1 and an intercept of $-\varphi_2 \cdot \varphi_3 \cdot \chi'_{23}$.

Jan-Chan Huang [Huang, 2003] and with R. Deanin [Huang & Deanin, 2004] rearranged equation (12) into the following form:

$$\frac{\chi_{1m}}{V_1} = \frac{\varphi_2 \cdot \chi_{12} + \varphi_3 \cdot \chi_{13}}{V_1} - \frac{\varphi_2 \cdot \varphi_3 \cdot \chi'_{23}}{V_2} \tag{13}$$

The polymer-polymer interaction term can be determined from the intercept at $\left(\dfrac{\varphi_2 \cdot \chi_{12} + \varphi_3 \cdot \chi_{13}}{V_1}\right) = 0$. This modification provided smaller standard deviations for the slope and the polymer-polymer interaction parameter.

Jan-Chan Huang [Huang, 2006] used also solubility parameter model to the study of the miscibility and thermodynamic properties of solutions by means of IGC. Because polymer–polymer mixtures have little entropy of mixing, the miscibility is largely decided by the sign of the heat of mixing. The determination of the heat of mixing becomes the key factor. The heat of vaporization is related to the solubility parameter, δ, of the liquid by the relation:

$$\delta = \left(\frac{\Delta E_{vap}}{V}\right)^{1/2} \tag{14}$$

where ΔE_{vap} is the energy of vaporization and V is the molar volume of the solvent.

The Flory–Huggins interaction parameter can be related to the solubility parameters of the two components by:

$$\chi = \left(\frac{V_1}{RT}\right) \cdot \left(\delta_1 - \delta_2\right)^2 \tag{15}$$

where δ_1 and δ_2 are the solubility parameters of the solvent and polymer, respectively, and V_1 is the volume of the solvent.

Guillet and co-workers [DiPaola-Baranyi & Guillet, 1978; Ito & Guillet 1979] have proposed IGC method for estimating of Flory–Huggins interaction parameter and solubility parameter for polymers by the modification of Eq. (15):

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1}\right) = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT}\right) \tag{16}$$

It is a straight line equation. The left-hand side contains the values of Flory–Huggins interaction parameter of test solute (see Eq. (2)), solubility parameter of test solute (δ_1)) and its molar volume. Plotting the left-hand side of such equation vs. solubility parameter of test solute (δ_1) one obtains the slope ($a = 2\delta_2/RT$) enabling the calculation of the solubility parameter of the examined material. This value should be equal to that found from the intercept and positive [Voelkel et al., 2009 (b)].

When a mixture is used as the stationary phase the solubility parameter of the mixture, δ_m, can be compared with the prediction of the regular solution method, which gives δ_m to be the volume average of the two components [Huang, 2006]:

$$\delta_m = \varphi_A \cdot \delta_A + \varphi_B \cdot \delta_B \qquad (17)$$

From this equation the formula of specific heat of mixing in the regular solution theory could be derived. A measurement of the solubility parameter of the polymer mixtures would then be a good indicator to predict their miscibility.

Huang [Huang, 2006] proposed a mechanism of probe dependency. When two polymers with specific interactions are brought together some functional groups interact with each other and are no longer available to the probes. Relative to the volume average of the pure components the probes will feel the mixture becomes lower in polar or hydrogen bonding interaction and more in nonpolar dispersive force. In other words, the mixture becomes more ''alkane-like''. The polar probes will be squeezed from the stationary phase and the specific retention volume decreased, which increases χ_{1m} through Eq. (5) then decreases χ'_{23} through Eq. (13). Therefore, polar probes have lower retention volume and χ'_{23}, and for n-alkane probes the change is less. This difference between probes is exhibited as the probe dependency.

4. Applications

Authors examined many polymeric materials filled with modified silica or other inorganic fillers. Our measurements were carried out with the use of Chrom5 (Kovo, Prague, Czech.Rep.) gas chromatograph equipped with a flame ionisation detector. Some of the results were presented here.

4.1 Flory-Huggins parameters for polylactic acid compositions

For composition of polylactic acid (P, M=55000), containing different amount (5, 10, 15% wt) of modified silica (B2 and B5) [Jesionowski, 1999] or modified carbonate-silicate fillers (N1 and N2) [Grodzka 2004] we calculated Flory-Huggins parameters χ_{12}^{∞} and χ'_{23}. The influence of the temperature and the amount and type of filler was examined. To eliminate the solvent dependence of χ'_{23} values (from basic Eq. 8) experimental data were recalculated according to Zhao-Choi procedure.

Small volumes (0.5μL) of vapour of the probes were injected manually to achieve the infinite dilution conditions. These were: n-pentane (C5), n-hexane (C6), n-heptane (C7), n-octane (C8), n-nonane (C9), dichloromethane (CH2Cl2), chloroform (CHCl3), carbon tetrachloride (CCl4), 1,2-dichloroethane (Ethyl. Chl.) (all from POCH, Gliwice, Poland).

Values of χ_{12}^{∞} parameter for P-15N1 (it denotes the composition of polylactic acid with 15% of N1 filler) composition we presented in Figure 2. We obtained almost the same values of χ_{12}^{∞} parameter for other investigated compositions.
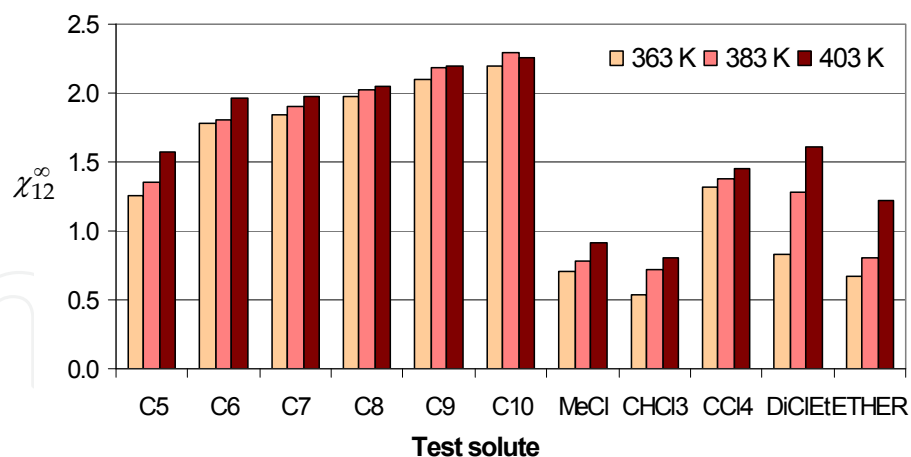
Fig. 2. Values of Flory-Huggins χ_{12}^{∞} parameter for P-15N1 composition

The lowest values of χ_{12}^{∞} parameter were obtained for dichloromethane (MeCl) and chloroform (CHCl3) as the test solute. Values calculated for compositions were almost always lower than those found for pure components, i.e. polymer and/or filler separately. The increase of temperature decreased values of χ_{12}^{∞} only for P-5B5 system, indicating the increase of interactions between composition and test solute. For the other compositions the increase of temperature increased values of χ_{12}^{∞} parameter.

The influence of the amount and type of filler was also examined. The change of these two factors also lead to the changes in the solute-composition interactions (Fig. 3). The influence of the amount of the filler is different for various compositions. For composition with N1 filler (carbonate-silicate filler modified with N-2-aminoethyl-3-aminopropyl-trimethoxysilane) the strongest interaction with solvent was found for the composition containing 5% of the filler. However, for P-N2 the most active is the composition with 15% addition of N2 (carbonate-silicate filler modified with n-octyltriethoxysilane).
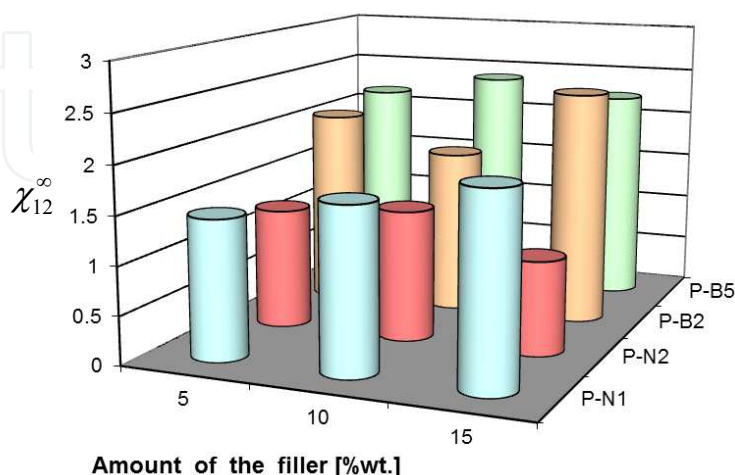
Fig. 3. The influence of the type and the amount of the filler [% wt.] on χ_{12}^{∞} parameters at 403K

Determined values of χ_{23}' depend on the type of the test solute used in IGC experiment (Fig. 4). Influence of the amount of the filler on the Flory-Huggins parameter χ_{23}' was examined and some results are presented in Figure 4. It is depended on test solute used in our study. For C5-C7 and CHCl3 and CCl4 we obtained the lowest values for 5% of N1 filler. For the other solutes – the strongest interaction are observed between polymer and 15% of the filler. Generally, the strongest interaction between components were observed for compositions with 5% of the filler.
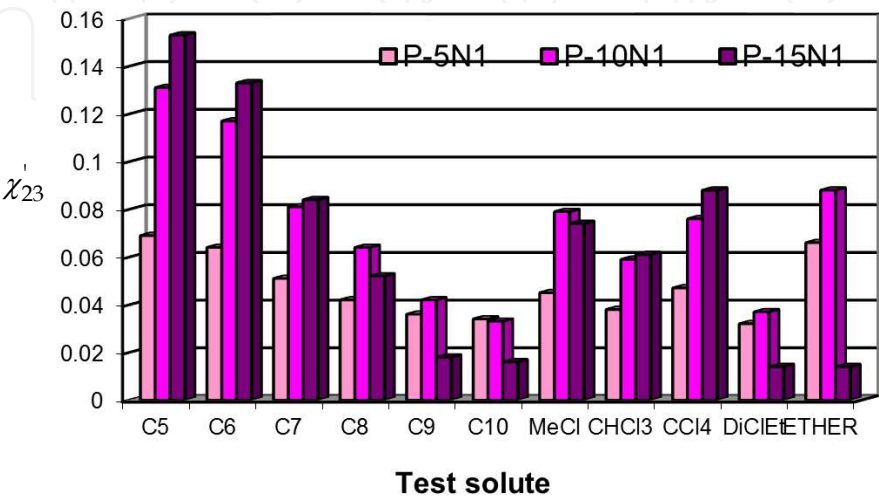
Fig. 4. Values of Flory-Huggins χ_{23}' parameter for compositions with 5%, 10% or 15% of filler

To eliminate the solvent dependence of χ_{23}' values (from basic equation) experimental data were recalculated according to Zhao-Choi procedure (Eq. 12). Values of $ZC\chi_{23}'$ parameter are presented in Figure 5. In all cases only one value for each composition was obtained. All $ZC\chi_{23}'$ values indicated the presence of strong or medium interaction between the modified filler and polymer matrix. This observation is consistent with that formulated after analysis of χ_{23}' data found for most of test solutes in the classic procedure.
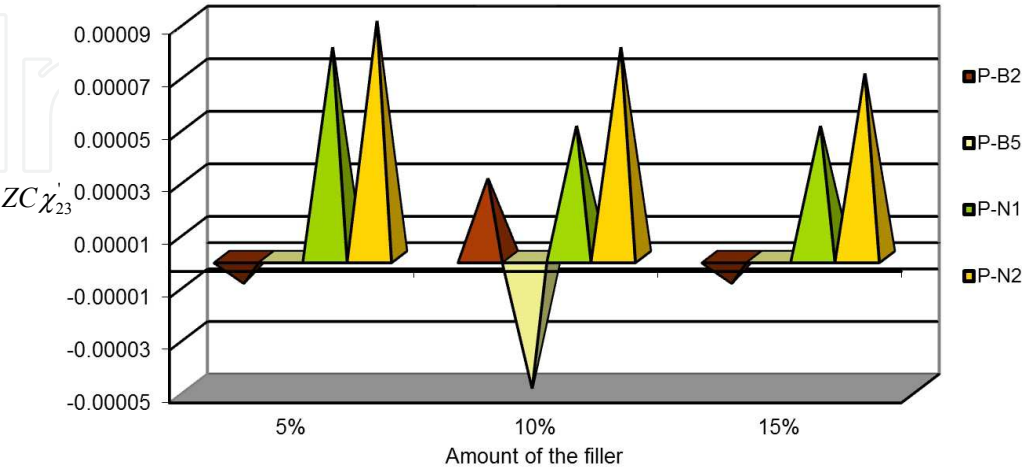

Fig. 5. Values of Flory-Huggins $ZC\chi_{23}'$ parameter for all compositions calculated according to Zhao-Choi procedure

It is worth to note that the increase of the filler content does not enhance the magnitude of interactions. Most often limited (rather negligible) decrease of polymer-filler interactions was observed.

4.2 Chemometric evaluation of IGC data

Principal Component Analysis (PCA) became a popular technique in data analysis for classification for pattern recognition and dimension reduction. It can reveal several underlying components, which explain the vast majority of variance in the data [Héberger, 1999; Malinowski, 1991; Héberger et al., 2001]. The principle is to characterize each object (rows in the input matrix) not by analyzing every variable (columns of the input matrix) but projecting the data in a much smaller subset of new variables (or principal component scores). PCA should facilitate the overcoming of the problem connected with the solute dependence of χ'_{23} parameter.

Values of Flory–Huggins χ'_{23} parameter expressing the magnitude of interactions between the polymer matrix and filler strongly depend on the type of test solute being used in IGC experiment (see Fig. 4). It causes the difficulties in the analysis of the influence of the type and amount of the filler onto the magnitude of these interactions. Such analysis is possible with the help of PCA technique [Voelkel et al., 2006] as presented in Fig. 6 for systems of polyurethane (PU) with modified silica fillers (B2). Materials used in experiments were described elsewhere [Milczewska & Voelkel 2002; Milczewska, 2001]. The magnitude of interactions is similar (the corresponding points belong to one – large cluster) for most of samples. Outside this large cluster the points correspond mainly to the compositions with 5 or 20% of the filler.
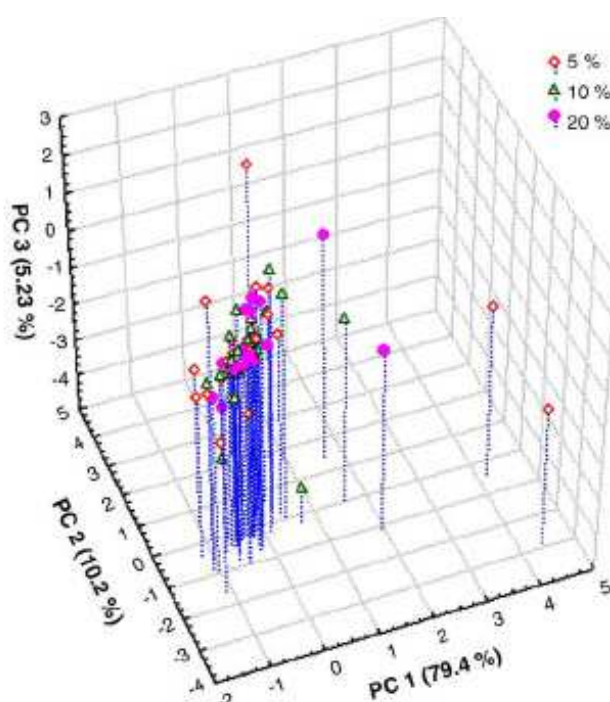

Fig. 6. Scatterplot for Polyurethane (PU) systems [Reprinted from Voelkel et al., 2006 with permission from Elsevier]

IGC procedures discussed earlier allow eliminating the test solutes dependence of χ'_{23} values. However, very often the relatively significant error of the determination was reported.

Values of χ'_{23} parameter calculated according to Zhao–Choi procedure for the examined polymeric composition are presented in Table 1. All values are negative and close to zero. It indicates the existence of polymer–filler interaction although their strength is limited.

Filler	PU-B2 compositions		
	PU+5%	PU+10%	PU+20%
IB2	$-2*10^{-5}$	$-2*10^{-5}$	$-2*10^{-5}$
IIB2	$-4*10^{-5}$	$-6*10^{-5}$	$-3*10^{-5}$
IIIB2	$-6*10^{-5}$	$-3*10^{-5}$	$-7*10^{-5}$
IVB2	$-3*10^{-5}$	$-1*10^{-5}$	$-7*10^{-5}$
VB2	$-7*10^{-5}$	$-3*10^{-5}$	$-1*10^{-5}$

Table 1. Values of χ'_{23} parameter calculated by Zhao-Choi method for B2-PU compositions [Reprinted from Voelkel et al., 2006 with permission from Elsevier]

The differences of the magnitude of polymer–filler interactions are significant as the error of determination is equal to approximately $2.5*10^{-7}$, i.e. it is at least two orders lower than the determined χ'_{23} values. However, collection of retention data for all test solutes is somewhat time-consuming. It would be useful to select the test solutes carrying the statistically valid information, applied these species in IGC experiments and further use their retention data in calculations of χ'_{23} from Zhao–Choi procedure. The problem was: how the reduction of the number of test solutes will influence the χ'_{23} values as well as error of their determination.

For all PU compositions PCA made possible using three - four test solutes (C6, C8, MeCl and CCl4) for determination of interaction parameters. Recalculating of χ'_{23} from Zhao–Choi procedure for selected test solutes gave values presented in Table 2.

Comparison of values of χ'_{23} calculated by Zhao-Choi method before and after PCA selection of solutes is presented on Figure 7. Corrected values are lower or higher than these found for all test solutes, but they indicate the presence or absence of interaction.

Filler	PU-B2 compositions		
	PU+5%	PU+10%	PU+20%
IB2	$-3*10^{-5}$	$-2*10^{-5}$	$-2*10^{-5}$
IIB2	$-3*10^{-5}$	$-5*10^{-5}$	$-3*10^{-5}$
IIIB2	$-5*10^{-5}$	$-3*10^{-5}$	$-5*10^{-5}$
IVB2	$-2*10^{-5}$	$0*10^{-5}$	$-7*10^{-5}$
VB2	$-4*10^{-5}$	$-1*10^{-5}$	$-1*10^{-5}$
Error ~ $2.5*10^{-7}$			

Table 2. Values of χ'_{23} parameter for B2-PU compositions calculated by Zhao-Choi method after PCA selection of solutes [Reprinted from Voelkel et al., 2006 with permission from Elsevier]
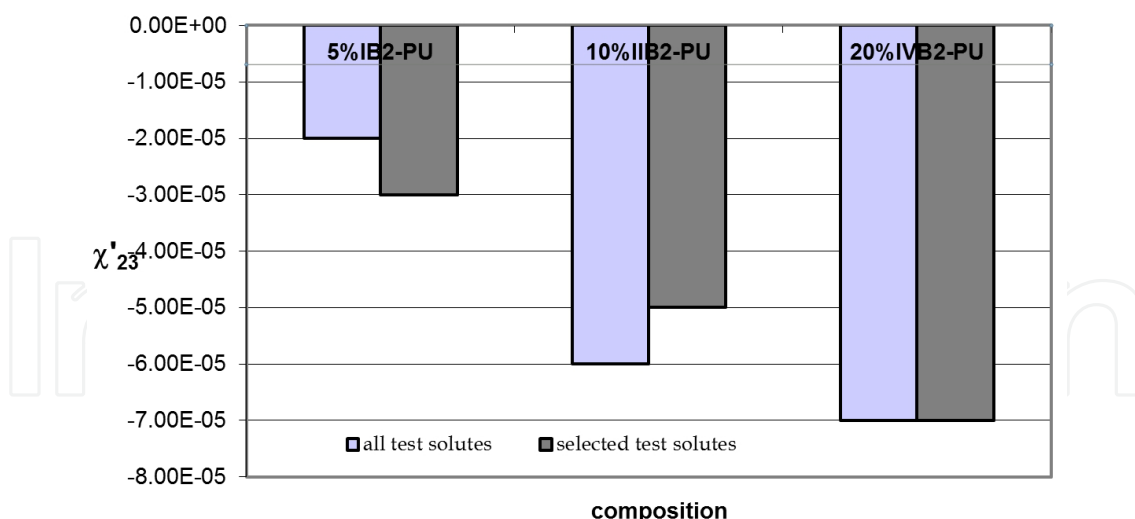
Fig. 7. Comparison of χ'_{23} calculated by Zhao–Choi procedure before and after PCA selection of test solutes for PU [Reprinted from Voelkel et al., 2006 with permission from Elsevier]

PCA enabled the significant reduction of the number of test solutes required for the proper determination of Flory–Huggins parameter and further the reduction of time required for proper characterization of examined material.

5. Summary

Inverse gas chromatography method has been found to be an effective tool for measurement of the magnitude of interaction (χ_{12}^{∞} interaction material – test solute) in polymers at different temperatures. From technological point of view χ'_{23} is more interesting. This parameter can be used as indicator of the miscibility of the polymer blend.

Drawback of χ'_{23} estimated by classical procedure is the test solute dependence. The procedure of its elimination proposed by Zhao-Choi seems to be most appropriate. It leads to realistic values of χ'_{23} with low error of determination. The full procedure of χ'_{23} .with the use of large series of the test solutes might be time-consuming. The use of chemometric analysis enabled the reduction of the number of the test solutes without loss of information. One may expect further application of IGC in examination of polymer materials.

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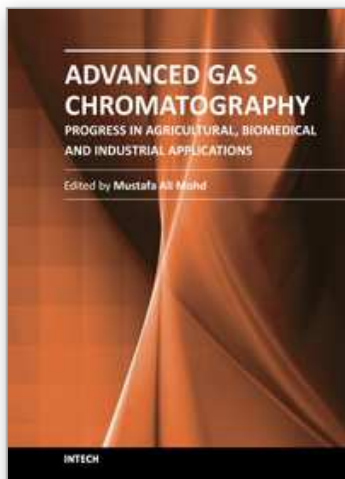
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Progress in agricultural, biomedical and industrial applications' is a compilation of recent advances and developments in gas chromatography and its applications. The chapters cover various aspects of applications ranging from basic biological, biomedical applications to industrial applications. Book chapters analyze new developments in chromatographic columns, microextraction techniques, derivatisation techniques and pyrolysis techniques. The book also includes several aspects of basic chromatography techniques and is suitable for both young and advanced chromatographers. It includes some new developments in chromatography such as multidimensional chromatography, inverse chromatography and some discussions on two-dimensional chromatography. The topics covered include analysis of volatiles, toxicants, indoor air, petroleum hydrocarbons, organometallic compounds and natural products. The chapters were written by experts from various fields and clearly assisted by simple diagrams and tables. This book is highly recommended for chemists as well as non-chemists working in gas chromatography.

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