Inverse Gas Chromatographic Examination of Polymer Composites

Adam Voelkel*, Beata Strzemiecka, Kasylda Milczewska, Zuzanna Okulus

Abstract: Inverse gas chromatographic characterization of resins and resin based abrasive materials, polymer-polymer and polymer-filler systems, as well as dental restoratives is reviewed.

Keywords: surface activity, polymer-polymer interactions, adhesion, dental restoratives, inverse gas chromatography

1 Introduction

Inverse gas chromatography (IGC) was introduced in 1967 by Kiselev [1], developed by Smidsrød and Guillet [2], and is still being improved. Its popularity is due to its simplicity and user friendliness. Only a standard gas chromatograph is necessary [3] although more sophisticated equipment has been advised. “Inverse” relates to the aim of the experiment. It is not separation as in classical GC, but examination of the stationary phase properties. Test compounds with known properties are injected onto the column containing the material to be examined. Retention times and peak profiles determine parameters describing the column filling. IGC makes possible polymer and composite study at different temperatures and humidities [4-6]. Polymer examination below the glass transition temperature ($T_g$) allows surface characterization, which can then be used to monitor surface changes occurring during chemical modification. For liquids, IGC can determine the Flory-Huggins interaction ($\chi^{12}$ and/or $\chi^{13}$), solubility ($\delta$), and three-dimensional Hansen solubility parameters. These allow prediction of polymer mutual solubility, miscibility of composite components and/or interactions between them, and behavior during technological processes.

This paper reviews the examination of various polymer-containing systems by inverse gas chromatography.

2 Discussion

2.1 Surface energy and adhesion

IGC is useful for surface energy determination of solid polymers and fillers. Solid surface energy of consists of dispersive ($\gamma_d^S$, from van der Waals forces) and specific ($\gamma_{sp}^S$, from acid-base interactions) components:

$$\gamma_s = \gamma_d^S + \gamma_{sp}^S$$

(1)

$\gamma_d^S$ for solids can be calculated according to several methods [7]; one of the most often used is that of Schultz-Lavielle [8-12]:

$$R \cdot T \cdot \ln V_n = 2 \cdot N \cdot a \cdot \sqrt{\gamma_d^S \cdot \gamma_l^p} + C$$

(2)

where:

$R$ = gas constant, 8.314 [J mol$^{-1}$ K$^{-1}$];

$T$ = temperature [K];

$V_n$ = net retention volume [m$^3$];

$N$ = Avogadro’s number, $6.023 \times 10^{23}$ [1 mol$^{-1}$];

$a$ = adsorbate cross sectional area [m$^2$];

$\gamma_d^S$ = surface free energy dispersive component [mJ m$^{-2}$];

$\gamma_l^p$ = liquid probe surface tension dispersive component [mJ m$^{-2}$];

$C$ = constant.

Retention data for polar and non-polar test compounds are necessary to quantify the surface acidic and basic properties ($\gamma_s^+$, $\gamma_s^-$) $\gamma_s^+\gamma_s^-$ according to the Good-van Oss concept [13]:

$$\Delta G_{sp} = 2 \cdot N_A \cdot a \cdot \left((\gamma_l^p \cdot \gamma_s^-)^{1/2} + (\gamma_l^p \cdot \gamma_s^+)^{1/2}\right)$$

(3)
\( y_a^+ \) and \( y_d^+ \) are the electron acceptor and donor parameters of the probe molecules. \( \Delta G^\text{sp} \) is the specific component of the polar compound’s Gibbs free energy of adsorption. Its determination has been described [79]. \( y_a^+ y_d^- \) Dichloromethane (DM) and ethyl acetate (EA) can be used as test compounds to determine \( y_a^+ \) and \( y_d^- \). DM is a monopolar acid with \( y_{DM}^- \) of 0.0 mJ m\(^{-2}\). Eq. (3) then reduces to:

\[
\gamma_s^+ = \frac{\Delta G_{DP}^{sp}}{(4 \cdot N_A^2 \cdot a_{DM}^0 \cdot \gamma_{DM}^-)}
\]  

(4)

\( y_a^+ \) has been reported to be 5.2 mJ m\(^{-2}\) [14]. Similarly, EA is a monopolar base and \( \gamma_{EA}^- \) is 0.0 mJ m\(^{-2}\). Thus, \( y_s^- \) for the solid can be calculated:

\[
\gamma_s^- = \frac{\Delta G_{DP}^{sp}}{(4 \cdot N_A^2 \cdot a_{EA}^0 \cdot \gamma_{EA}^-)}
\]  

(5)

\( \gamma_{EA}^- \) is 19.2 mJ m\(^{-2}\) [14]. However, in the literature there are different values for test compound surface free energy components and parameters [15]. Van Oss gave \( y_l^- \) of 6.2 mJ m\(^{-2}\) for EA, which differs from that in [16]. Moreover, \( y_l^- \) for dichloromethane (DM) is not given therein, but only that for chloroform (CH; 1.5 mJ m\(^{-2}\)) [16].

We have calculated \( y_s^+ K_A, y_s^- \) for the materials studied here using \( y_l^+ K_A, y_l^- \) from both these sources. The sensitivity of \( y_s^+ K_A, y_s^- \) for EA, \( \gamma_{sp} \), \( W_a^{ab} \) and \( W_d \) to the assumed \( y_l^+ K_A, y_l^- \) for the acidic and basic parameters has been discussed [17]. \( y_s^+ \) \( y_s^- \). The \( y_s^+ \) values calculated from van Oss’ data [16] were three times higher than those calculated according to data from [14]. The \( y_s^- \) values \( y_s^- \) calculated from van Oss’ data [16] were from 1/3 to 1/5 those calculated from data in [14]. However, the trends in both parameters were independent of which was used. The \( y_s^+ \) were similar as well as the \( W_a^{ab} \) and \( W_d \). Parameters estimated by IGC should not be treated as absolute, but they are very useful for materials comparisons.

There are several methods for solid surface energy determination; contact angle measurement is most often used \( y_s^- \) [17]. The use of different polar and nonpolar liquids enables determination of the Lifshitz-van der Waals (\( \gamma_{LW}^\text{sp} \)) and the Lewis acid-base (\( \gamma_{ab}^\text{sp} \)) components of \( y_s^- \). Moreover, the electron-acceptor (\( y_s^+ \)) and electron-donor (\( y_s^- \)) parameters of the acid-base component can be determined if the components of the liquid surface free energy are known.

However, this method suffers from some limitations, e. g. the diameter of the liquid drop affects the results [17] and the solid surface must be smooth [18,19]. The solids are frequently powders and it is impossible to prepare a flat and smooth surface. The Washburn method [21] of powder surface energy estimation suffers from difficulty in homogeneously packing the powder into tubes [17].

IGC seems a much better method for studying solid powders, especially for such solids as very hard 1–0.25 mm abrasive grains [22]. It is impossible to form a disk and the Washburn method might be inaccurate. Indirect estimation of the contact angle is impossible due to the grains’ irregular shape and small size. IGC made it possible to determine their surface free energy. The authors of this review have also used IGC to characterize carbon black powders [23]. Very often insufficient material is available for contact angle measurement. IGC requires only several mg.

The surface energy of connected solids determines their strength (work) of adhesion, \( W_a \), resulting from dispersive (van der Waals) and acid-base interactions.

\[
W_a = W_d^a + W_a^{ab}
\]  

(6)

\( W_d^a \) is the dispersive component and \( W_a^{ab} \) is the acid-base component. Eq. (6) can be used to determine the work of adhesion in solid polymer-filler system such as abrasive-hardened resin binder [22,24] or polyurethane-carbon black [25]. \( W_d^a \) can be calculated by [26–29]:

\[
W_d^a = \frac{2 \cdot y_{df}^d \cdot \gamma_{df}^{sp}}{\sqrt{y_{df}^d \cdot y_{sp}^{df}}} \]  

(7)

\( y_{df}^d \) denote the dispersive components of the filler (f) and resin (p) free surface energies. \( W_a^{ab} \) is the component due to acid-base interactions:

\[
W_a^{ab} = 2 \cdot \left( (y_{sf}^+ \cdot y_{sp}^-)^{1/2} + (y_{sf}^- \cdot y_{sp}^+)^{1/2} \right)
\]  

(8)

\( W_a^{ab} \) and \( y_{sf}^+ \), \( y_{sf}^- \) are the acidic and basic parameters of the polymer surface (p) describing its electron acceptor and electron donor abilities. \( y_{sf}^+ \), \( y_{sf}^- \) denote the same characteristics of the filler (f). \( W_d \) is the filler work of cohesion, is calculated as a sum of dispersive (\( W_d^a \)) and specific (\( W_a^{ab} \)) components in the same way as the work of adhesion [29]:

\[
W_{coh}^d = 2 \cdot \sqrt{y_{sf,\text{filler}}^d \cdot y_{sp,\text{filler}}^{df}}
\]  

(9)

\[
W_{coh}^{ab} = 2 \cdot \left( (y_{sf,\text{filler}}^+ \cdot y_{sp,\text{filler}}^-)^{1/2} + (y_{sf,\text{filler}}^- \cdot y_{sp,\text{filler}}^+)^{1/2} \right)
\]  

(10)
If the ratio of $W_a/W_{coh}$ is close to 1 the filler cohesion forces and filler-polymer adhesion forces are in balance.

### 2.2 Polymer-polymer interactions

The usefulness of IGC for determining polymer–small molecule interactions is well established. The Flory-Huggins interaction parameter $\chi_{12}$ is a measure of the free energy of interaction between the probe and the material tested. Experimental retention parameters (e.g. $V_g$ – specific retention volume) can be converted to Flory-Huggins parameters [30]:

$$\chi_{12} = \frac{1}{\phi_2 \cdot \phi_3} \left( \ln \frac{V_{1,m}}{V_i} - \phi_2 \cdot \frac{\rho_1}{\rho_{1,s}} \cdot \ln \left( \frac{\rho_{1,s}}{\rho_1} \right) - \phi_3 \cdot \frac{V_i}{V_i'}\right)$$  \hspace{1cm} (11)

where: 1 denotes the solute and 2 or 3 denotes polymer or filler, $M_1$ the molecular weight of the solute, $p_{1,s}$ the saturated solute vapour pressure, $B_{11}$ the solute second virial coefficient, $V_i$ the molar volume, $\rho_1$ the density, $R$ the gas constant, and $V_g$ the specific retention volume.

For a filled polymer, Eq. (11) can be rearranged [31,32]:

$$\chi_{12} = \frac{1}{\phi_2 \cdot \phi_3} \left( \ln \frac{273.15 \cdot R}{p_1 \cdot V_i \cdot M_1} - \frac{p_{1,s}}{R \cdot T} \cdot (B_{11} - p_{1,s}) + \ln \left( \frac{\rho_{1,s}}{\rho_1} \right) - \left( 1 - \frac{V_i'}{V_i} \right) \cdot \phi_3 \cdot \left( 1 - \frac{V_i'}{V_i} \right) \cdot \phi_3 \right)$$  \hspace{1cm} (12)

where $\phi_2$ and $\phi_3$ are the polymer and filler volume fractions and $m$ refers to the composite.

Inverse gas chromatography can also be used to characterize composite component interactions (polymer-polymer, polymer-filler, filler-filler), expressed by the Flory-Huggins parameter $\chi_{23}$ [33,34]:

$$\chi_{23} = \frac{\chi_{23}^{e} \cdot V_i^e}{V_i} = \frac{1}{\phi_2 \cdot \phi_3} \left( \ln \frac{V_{e,m}^{e}}{W_2 \cdot V_2 + W_3 \cdot V_3} - \phi_2 \cdot \ln \frac{V_{e,m}^{e}}{W_2 \cdot V_2} - \phi_3 \cdot \ln \frac{V_{e,m}^{e}}{V_3} \right)$$  \hspace{1cm} (13)

Here, the second subscript of $V_g$ identifies the nature of the column.

To obtain $\chi_{23}^{e}$ for a polymer blend or composition utilizing IGC, $\chi_{12}$ values for all components must be known. Therefore, three columns are usually prepared: two containing the single components and the third containing their composite. A further three columns containing different composites can also be prepared if the effect of composite proportions is to be examined. These columns should be tested using identical temperature, flow rate, inlet pressure, and test solutes [35]. The usual sign convention is assumed; i.e., a large positive value indicates unfavourable interaction, a low value indicates favourable interaction, while a negative value indicates a rather strong specific interaction.

The effects of three variables on the polymer/filler interaction parameter $\chi_{23}$ were examined:
- the type of filler
- the amount of filler
- the test solute.

Although not predicted by the theory, $\chi_{23}$ values commonly depend on the solute chemical structure [36]. This has been interpreted as due to preferential interactions of the test solute with one of the components.

![Figure 1: Filler influence on $\chi_{23}$ (PE2 – polyethylene; B – fillers: silica modified with: N-2-aminoethyl-3-aminopropyltrimethoxysilane (B2), 3-aminopropyltriethoxysilane (B3), 3-mercaptopropyl-trimethoxysilane (B4), n-octyltriethoxysilane (B5)).](image-url)
Milczewska and Voelkel [34,37] discussed some methods of creating a probe-independent interaction parameter. Zhao and Choi [31,32] proposed a ‘common reference volume’ ($V_o$, the smallest polymer repeat unit molar volume) to remove the problem. Their definition of $\chi$ differed from the traditional definition by the ratio of reference to probe volume ($V_o/V_1$). When a common reference volume was used, the data conformed to the ternary Flory-Huggins lattice theory and unique $\chi_{23}$ values were obtained if the solvents used satisfied the zero $\Delta \chi$ criterion.

Zhao and Choi proposed two equations for $\chi_{23}$:

$$\chi_{23} = \frac{V_2}{V_1} \left( \ln \frac{273.15 \cdot R}{M_2 \cdot V_2 \cdot \Phi_1} - 1 \right) - \left( \frac{1 - \Phi_2}{V_2} \Phi_1 \right) \frac{\chi_{12}}{\Phi_1} - \left( \frac{1 - \Phi_3}{V_2} \Phi_1 \right) \frac{\chi_{13}}{\Phi_1} \left( \frac{B_2 - V_2}{R \cdot T} \right) \Phi_2$$

(14)

and

$$\chi_{1w} = \Phi_2 \cdot \chi_{12} + \Phi_3 \cdot \chi_{13} - \Phi_2 \cdot \Phi_3 \cdot \chi_{23}$$

(15)
Eq. (15) predicts that a plot of $X_{1m}$ versus $(\phi_2 \cdot X_{1s} + \phi_3 \cdot X_{1s})$ will give a straight line with slope 1 and intercept $(\phi_2 \cdot \phi_3 \cdot X_{1s})$.

### 2.2 Activity of tooth tissue and dental restorative

Another interesting application of inverse gas chromatography is the examination of polymeric dental restorative materials’ surface properties. Preceded by the removal of infected tissue, their application is the only way to prevent dental caries – which affects people all over the world [38]. Caries consists of tooth destruction by demineralization of the inorganic part and destruction of the organic one by microorganisms [39]. Replacement restores tissue continuity and function.

Polymers are used in all fields of dentistry [40]. Polymeric restoratives include a very wide spectrum of types, including composites, glass-ionomer cements, resin-modified glass-ionomer cements and compomers [41]. All have very complex compositions; their properties reflect this complexity. Composites consist mainly of an organic matrix and inorganic filler in varying proportion. In many cases a coupling agent to improve their adhesion is required. Polymerization initiators allow hardening by blue light photopolymerization [41-47]. Glass-ionomer cements are composed of polyacrylic acid, fluorooluminosilicate glass, water, and tartaric acid. Setting between filler and matrix occurs by acid-base reaction [41,48]. Resin-modified glass-ionomer cements contain methacrylate resin. This allows a dual curing method – the first, a conventional glass-ionomer acid-base reaction starts upon mixing, while the second is initiated by light as in conventional composites [41,48]. Compomers are polyacid-modified composites, in which setting occurs first by photopolymerization and subsequently by a slow acid-base reaction after water sorption [41,49].

All should adhere well to tooth tissues and prevent microorganism adhesion. Both behaviors crucially depend on the surface properties [50]. Dental caries starts with a bacterial biofilm (dental plaque) covering the tooth surface [51-53]. High surface energy contributes to this phenomenon. $\gamma_s^C$ is the most important parameter because low values significantly reduce bacterial ability to adhere in comparison with materials with high $\gamma_s^C$ [54-55].

Rüttermann et al. investigated dental composite surface energy [54-55] by the contact angle method. This method is most popular but a false result can be obtained if the surface is not smooth [18], and it is very important to use the same drop diameter [56].

Inverse gas chromatography avoids these problems and has been used to estimate materials’ susceptibility to biofilm formation. Both dispersive [57-58] and specific [59] surface energy components have been determined for glass-ionomer cements, which are known for their ability to absorb water. These show highest surface activity (strongest dispersive interactions) at lowest humidity [57-58] and increased wet storage time increases their surface activity [58]. The surface is strongly basic and acid-base interactions decrease at higher humidity [59]. This information is important in applications. This suggests that IGC will also be successful in examination of other, potentially more stable materials applied as dental fillings.

The surface energy of bovine tooth tissues was also examined by means of IGC. Tissue type (dentin or
enamel), site (crown or root) and storage conditions (dry or wet) affect the dispersive and specific interactions. In all cases the dispersive component dominates the specific component. Differences in surface energy parameters strongly correlate with composition, specific surface area and surface morphology (e.g. pore content) [60].

Dental restorative should strongly adhere so the connection is durable and filling replacement is unnecessary. Weak attachment results in microcracks and microleakage, the main cause of secondary caries [61]. Work of adhesion between restorative and tooth depends on the surface energies of both [22].

Our preliminary IGC study determined the surface energy components of the commercial dental composite Charisma and untreated bovine tooth [62]. Adhesion differed between Charisma and the two tooth tissues examined. Further investigation will be conducted for teeth after etching, conditioning, priming and bonding; treatments designed to improve adhesion [63]. Treated tooth surface energies may clarify which steps impact most on adhesion. Comparison of IGC and mechanical shear bond strength test results will enable predicting the adhesion in designing dental restoratives.

3 Conclusions

Inverse gas chromatography is promising for characterization of complex polymeric systems, and disadvantages of the contact angle technique may be overcome. Determination of surface energy, work of adhesion, and the magnitude of polymer-filler interactions give insight into the behavior of technologically important systems.

Acknowledgment: This work was supported by 03/32/DS PB/0500.

References

[1] Kiselev A.V., In: Giddings J. C., Keller R.A. (Eds.), Advances in Chromatography, Marcel Dekker Co., New York 1967
[2] Smidsrød O., Guillet J. E., Study of Polymer-Solute Interactions by Gas Chromatography, Macromolecules, 2, 1976, 2, 272-282.
[3] Kunaver M., Zadnik J., Planinšek O., Srčič S., Inverse gas chromatography - A different approach to characterization of solids and liquids, Acta Chim. Slov., 2004, 51, 373-394.
[4] Strzemiecka B., Kolodziejej J., Kasperkowiak M., Voelkel A., Influence of relative humidity on the properties of examined materials by means of inverse gas chromatography, J. Chromatogr. A, 2013, 1271, 201-206.
[5] Voelkel A., Strzemiecka B., Application of Inverse Gas Chromatography in the Characterization of Raw Material Used in Manufacturing of Abrasive Materials, Colloids Surf. A: Physicochem. Eng. Aspects, 2006, 280, 177-181.
[6] Voelkel A., Strzemiecka B., Characterization of Fillers Used in Abrasive Articles by Means of Inverse Gas Chromatography and Principal Component Analysis International J. Adhes. Adhes., 2007, 27, 188-194.
[7] Voelkel A., Strzemiecka B., Adamska K., Milczewska K., Inverse gas chromatography as a source of physiochemical data, J. Chromatogr. A, Review, 2009, 1216, 1551-1566.
[8] Voelkel A., IGC what is this?, In: A. Dąbrowski, Tertykh V. A. (Eds.), Adsorption on New and Modified Inorganic Sorbents, Studies in Surface Science and Catalysis, Elsevier Science B. V., Amsterdam, 1996, pp. 465-477.
[9] Belgacem M. N., Gandini A., Inverse Gas Chromatography as a Tool to Characterize Dispersive and Acid-Base Properties of the Surface of Fibers and Powders, in: Pefferkorn E. (Ed.), Interfacial Phenomena In Chromatography, Marcel Dekker, Inc., New York, 1999, pp. 41-124.
[10] Bogilò V. I., Shkilev V. P., Voelkel A., Determination of surface free energy components for heterogeneous solids by means of inverse gas chromatography at finite concentrations, J. Mater. Chem., 1998, 8, 1953-1961.
[11] Schultz J., Lavielle L., Martin C., Propriétés de Surface des Fibres de Carbone Détérmìées par Chromatographie Gazèuse Inverse, J. Chimie Phys., 1987, 84, 231-237.
[12] Schultz J., Lavielle L., Martin C., Role of the interface on carbon fibre/epoxy composites, J. Adhesion, 1987, 23, 45-60
[13] van Oss C.J., Good R., Chaudhury M., Additive and nonadditive surface tension components and the interpretation of contact angles, Langmuir, 1988, 4, 884-891.
[14] Das C. S., Larson I., Morton D. A.V., Stewart P. J., Determination of the polar and total surface energy distributions of particulates by inverse gas chromatography, Langmuir, 2011, 27, 521-523.
[15] Jańczuk B., Bialopiotrowicz T., Zdziennicka A., Some Remarks on the Components of the Liquid Surface Free Energy, J. Colloid Interface Sci. 1999, 211, 96–103.
[16] van Oss C. J., Interfacial Forces in Aqueous Media, Taylor & Francis Group, LLC, Boca Raton, London, New York, 2006.
[17] Abbasian A., Ghaffarian S. R., Mohammadi N., Fallahi D., Sensitivity of Surface Free Energy Analysis Methods to the Contact Angle Changes Attributed to the Thickness Effect in Thin Films, J. Appl. Polym. Sci., 2004, 93, 1972–1980.
[18] Costanzo P. M., Wu W., Giese R. F. Jr., van Oss C. J., Comparison between Direct Contact Angle Measurements and Thin Layer Wicking on Synthetic Monosized Cuboid Hematite Particles, Langmuir, 1995, 11, 1827-1830.
[19] Kowk D. Y., Gietzelt T., Grundke H.-J., Neumann A. W., Contact Angle Measurements and Contact Angle Interpretation. 1. Contact Angle Measurements by Axisymmetric Drop Shape Analysis and a Goniometric Sessile Drop Technique, Langmuir, 1997, 13, 2880-2894.
[20] Chibowski E., Perea-Carpio R., Problems of contact angle and solid surface free energy determination, Adv. Colloid Interface Sci., 2002, 98, 245-264.
[21] Chibowski E., Hołysz L., Use of the Washburn Equation for Surface Free Energy Determination, Langmuir, 1992, 8, 710-716.
[60] Okulus Z., Strzmiecka B., Czarnecka B., Buchwald T., Voelkel A., Surface energy of bovine dentin and enamel by means of inverse gas chromatography, Mater. Sci. Eng. C., 2015, 49, 382-389.

[61] Hikita K., Van Meerbeek B., De Munck J., Ikeda T., Van Landuyt K., Maida T., Lambrechts P., Peumans M., Bonding effectiveness of adhesive luting agents to enamel and dentine, Dental Materials, 2007, 23, 71-80.

[62] Okulus Z., Strzemecka B., Czarnecka B., Voelkel A., Determination of the adhesion between tooth and dental filling by inverse gas chromatography, In: Martín Martínez J.M., Suárez Bermejo J.C. (Eds.), 10th European Conference on Adhesion – Papers, Sociedad de Adhesión, Alicante, 2014, pp. 277-280.

[63] Swift E.J., Dentin/enamel adhesives: review of the literature, Pediatric Dentistry, 2002, 24, 456-461.