# Characterization of the interactions in polymer–filler systems by inverse gas chromatography

Kasylda Milczewska, Adam Voelkel*

*Institute of Chemical Technology and Engineering, Poznan University of Technology, Pl. M. Sklodowskiej-Curie 2, 60-965 Poznan, Poland*

## Abstract

Inverse gas chromatography (IGC) has been applied to observe the interactions in filled polymer–organic solvent as well as modified filler–polymer systems under conditions approaching infinite dilution of the volatile component. We investigated polyether–urethane–modified silica systems containing different kinds of modified silicas (filler) at 10% w/w loading. The fillers were modified with $N$-2-aminoethyl-3-aminopropyltrimethoxysilane (B2), 3-aminopropyltriethoxysilane (B3), 3-mercaptopropyl-trimethoxysilane (B4), $n$-octyltriethoxysilane (B5). The values of Flory–Huggins parameter $\chi_{12}^{\infty}$ calculated from the retention volumes indicate that interactions between filled polymer and solvent probe varied with type of the modifier and temperature. Authors propose to express the magnitude of modified filler–polymer interactions by Flory–Huggins $\chi_{23}'$ parameter. The influence of conditions of IGC experiment (temperature, the type of filler, the nature of test solute) on the evaluated parameters is presented and discussed.
© 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Polymer–filler interactions; Flory–Huggins parameter; Inverse gas chromatography; Alkanes; Chloroform; Carbon tetrachloride; Dichloroethane

## 1. Introduction

Guillet and Smidsrod [1] have shown that by the use of gas chromatography a number of interesting properties of the polymer could be revealed. Because the stationary phase is the phase of interest (in contrast to the conventional gas chromatography) the method is called inverse gas chromatography (IGC). This method was extensively used for the measurement and evaluation of the thermodynamic interactions of polymers (above their glass transition) with low-molecular mass probes.

Deshpande et al. [2] were the first to suggest the use of IGC for studying the polymer blends. Starting from Flory–Huggins expression for the change of free enthalpy of mixing $\Delta G_{\mathrm{mix}}$ extended to three-component systems, they proposed a method of elaboration of IGC data collected with the use of polymer blend leading to the polymer–polymer interaction coefficient.

### 1.1. Theory and calculations

In our study we will show that the Flory–Huggins theory can be useful in the characterization of the interaction in polymer–filler systems. We investigated the compositions of oligomeric polyether–urethane with modified silica at 10% loading.

The values directly measured by IGC were the retention times of solutes, $t_{\mathrm{R}}$, the mass of the

*Corresponding author. Tel.: +48-61-665-3687; fax: +48-61-665-3649.

*E-mail address:* adam.voelkel@put.poznan.pl (A. Voelkel).

stationary phase, $m_w$, the temperature of column $T$, the flow-rate, $F$. Then, the specific retention volume, $V_g$ can be computed from Ref. [3]:

$$V_g = \frac{3}{2} \cdot \frac{t'_R j F 273}{m_w T} \tag{1}$$

where: $t'_R = t_R - t_M$, $t_M$ is gas hold-up time, $j$ is the James–Martin coefficient [4].

At infinite dilution of the probe and for high-molecular mass of the stationary phase (in our case a filled polymer), the Flory–Huggins interaction parameter can be determined from Refs. [5–7]:

$$\chi^\infty_{12} = \ln\left(\frac{273.15R}{p^\circ_1 V_g M_1}\right) - \frac{p^\circ_1}{RT}\cdot(B_{11} - V^\circ_1) + \ln\left(\frac{1}{2}\right)$$
$$- \left(1 - \frac{V^\circ_1}{V^\circ_2}\right) \tag{2}$$

The suitable symbols were explained earlier [8].

If the parameters $\chi^\infty_{12}$ and $\chi^\infty_{13}$ are known (from IGC experiment with appropriate component "2" or "3") the interaction parameter $\chi'_{23}$ may be calculated from equation [9]:

$$\chi'_{23} = \frac{\chi^\infty_{23} V^\circ_1}{V^\circ_2} = \frac{1}{\varphi_2 \varphi_3}$$
$$\cdot \left(\ln\frac{V_{g,m}}{W_2 \nu_2 + W_3 \nu_3} - \varphi_2 \cdot \ln\frac{V_{g,2}}{\nu_2} - \varphi_3 \cdot \ln\frac{V_{g,3}}{\nu_3}\right) \tag{3}$$

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

$\chi'_{23}$ was used in the characterization of the series of polymer–polymer blend [9–12].

Aim of this paper was the application of Flory–Huggins parameter in characterization of polymer–filler composition. Activity of these compositions may be expressed by $\chi^\infty_{12}$ values, while polymer–modified filler interactions by values of $\chi'_{23}$ parameter.

## 2. Experimental

We investigated oligomeric polyether–urethane filled with different kind of modified silica at 10% loading. The fillers were modified with: N-2-amino-ethyl-3-aminopropyltrimethoxysilane (B2), 3-amino-propyltriethoxysilane (B3), 3-mercapto-propyl-trimethoxysilane (B4), n-octyltriethoxysilane (B5) (UNISIL, Tarnow, Poland). Content of modifier was equal to 1, 2, 3, 5, 10 parts:100 parts (w/w) of silica.

Measurements were carried out with the use of Chrom5 (Kovo, Prague, Czech Republic) gas chromatograph equipped with a flame ionisation detector. Dried helium was used as a carrier gas. Glass columns, 100 cm×0.4 mm I.D., were packed with the support coated with polymer or filled polymer. Polymer and modified silica filled polymer were coated from solution onto Chromosorb P AW DMCS (Sigma, St. Louis, USA) at 15% (w/w) loading. Columns packed only with the modified silica were also tested. Columns were conditioned under helium at maximum analysis temperature over night before use. Various chemical compounds were used as the test solutes in IGC experiments. Small volumes (0.5 μl) of vapour of the probes were injected manually to achieve the infinite dilution conditions. They were: n-pentane ($C_5$), n-hexane ($C_6$), n-heptane ($C_7$), n-octane ($C_8$), n-nonane ($C_9$), dichloromethane ($CH_2Cl_2$), chloroform ($CHCl_3$), carbon tetrachloride ($CCl_4$), 1,2-dichloroethane (Ethyl. Chl.) (all from POCH, Gliwice, Poland). Silicas used as fillers were precipitated and modified by A. Krysztafkiewicz and T. Jesionowski from Poznan University of Technology.

## 3. Results and discussion

Values of $\chi^\infty_{12}$ parameter as a measure of free energy of interactions between the probe and the examined material obtained for example systems were given below (Tables 1 and 2). Similar values of $\chi^\infty_{12}$ parameter were found for other compositions with modified fillers.

The parameter exhibited high values for solvents weakly interacting with the material while low values were found for strongly interacting components. Values of $\chi^\infty_{12}$ parameter, for dichloromethane and chloroform as a test solutes, obtained for compositions were almost always lower than those found for pure components. The decrease in $\chi^\infty_{12}$ is caused by the addition of filler into polymer. The best

Table 1
Flory–Huggins interaction parameter $\chi_{12}^{\infty}$ for B3 system (3% of modifier in filler)

| Test solute | Oligomer | | Filler (IIIB3) | | Composition (10% IIIB3) | |
|---|---|---|---|---|---|---|
| | 383 K | 403 K | 383 K | 403 K | 383 K | 403 K |
| $C_5$ | 0.1547 | −0.5272 | 1.1325 | 0.8006 | 0.4936 | 0.3733 |
| $C_6$ | 0.5326 | 0.2494 | 1.7169 | 1.5220 | 1.0296 | 0.8958 |
| $C_7$ | 0.6980 | 0.3701 | 1.7969 | 1.6519 | 1.0977 | 1.0624 |
| $C_8$ | 0.8513 | 0.6071 | 1.9175 | 1.8054 | 1.1989 | 1.1628 |
| $C_9$ | 0.9896 | 0.7642 | 2.0286 | 1.9311 | 1.2801 | 1.2670 |
| $CH_2Cl_2$ | −0.0437 | −0.2387 | 1.1596 | 1.1316 | −0.2581 | −0.2327 |
| $CHCl_3$ | −0.1765 | −0.2769 | 1.2895 | 1.2656 | −0.5563 | −0.4669 |
| $CCl_4$ | 0.3372 | 0.0627 | 2.0044 | 1.7712 | −0.1311 | −0.1271 |
| Ethyl. Chl. | 0.3333 | 0.1528 | – | – | – | – |

Table 2
Flory–Huggins interaction parameter $\chi_{12}^{\infty}$ for B5 system (3% of modifier in filler)

| Test solute | Oligomer | | Filler (IIIB5) | | Composition (10%IIIB5) | |
|---|---|---|---|---|---|---|
| | 383 K | 403 K | 383 K | 403 K | 383 K | 403 K |
| $C_5$ | 0.1547 | −0.5272 | 0.9856 | 0.8801 | 0.3974 | 0.2564 |
| $C_6$ | 0.5326 | 0.2494 | 1.3561 | 1.3367 | 0.9656 | 0.7896 |
| $C_7$ | 0.6980 | 0.3701 | 1.2577 | 1.2838 | 1.0741 | 0.9430 |
| $C_8$ | 0.8513 | 0.6071 | 1.2106 | 1.2417 | 1.1895 | 1.0935 |
| $C_9$ | 0.9896 | 0.7642 | – | – | – | – |
| $CH_2Cl_2$ | −0.0437 | −0.2387 | 0.7733 | 0.6904 | −0.2992 | −0.3016 |
| $CHCl_3$ | −0.1765 | −0.2769 | 0.9172 | 0.9648 | −0.5895 | −0.5651 |
| $CCl_4$ | 0.3372 | 0.0627 | 1.4928 | 1.5934 | −0.1796 | −0.2585 |
| Ethyl. Chl. | 0.3333 | 0.1528 | – | – | – | – |

results for polar probes (low $\chi_{12}^{\infty}$ values) were obtained when silica modified with $n$-octyltriethoxy-silane was used as filler.

The amounts of modifier in filler also lead to the changes in the solute–composition interactions. For the small amount of modifier (Fig. 1) we obtained
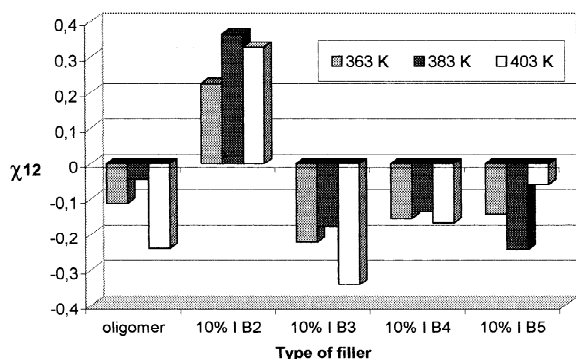
positive $\chi_{12}^{\infty}$ values for B2-filled polymer while for 3% of modifier negative values we obtained for all systems (Fig. 2). The increase of temperature decreased values of $\chi_{12}^{\infty}$ indicating the increase of interactions between composition and solute.

Values of Flory–Huggins parameter $\chi_{23}'$ express



Fig. 1. Dependence of $\chi_{12}^{\infty}$ parameter for dichloromethane on the type of filler and temperature (1 mass part of modifier).
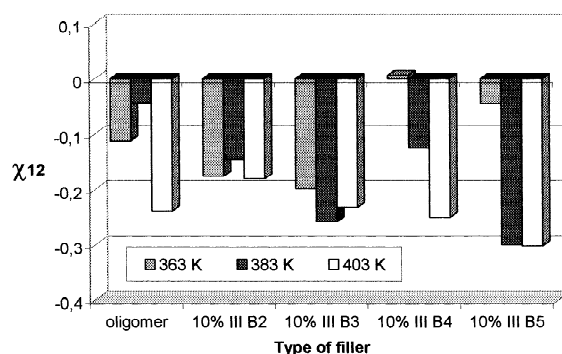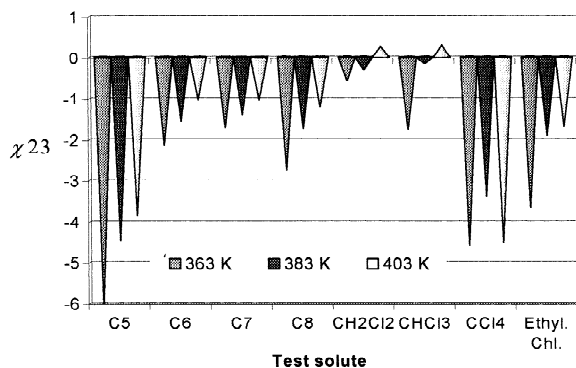


Fig. 2. Dependence of $\chi_{12}^{\infty}$ parameter for dichloromethane on the type of filler and temperature (3 mass parts of modifier).

Fig. 3. Values of $\chi'_{23}$ for different test solutes (10% IIB4).



Fig. 5. Influence of the amount of modifier in filler on the $\chi'_{23}$ parameter.

significant interactions between components of polymer/filler systems. For different solutes we obtained different values of $\chi'_{23}$ (Fig. 3). It is in agreement with literature [13,14], but not explained by Flory–Huggins theory. We compared $\chi'_{23}$ parameters (chloroform as the test solute) for all compositions (Fig. 4). The lowest values of $\chi'_{23}$ parameter occurred for composition with silica modified with *N*-2-aminoethyl-3-aminopropyltrimethoxysilane. The worst system (the weakest interactions) was PU-B5 composition.

In almost all cases $\chi'_{23}$ values were near zero. Strongly negative values couldn't be observed as it is impossible to discuss the miscibility between modified silica and polymer. Positive but close to zero val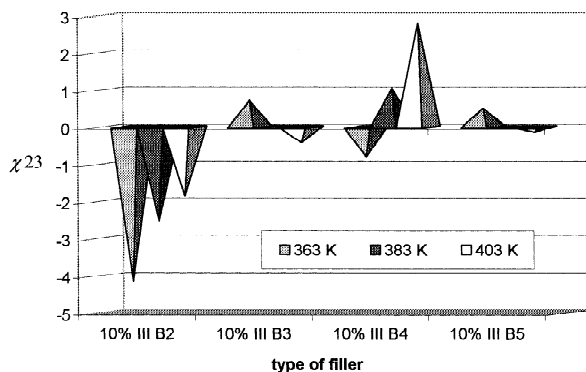ues of $\chi'_{23}$ indicate weak interactions between the components of the given system. Decrease of $\chi'_{23}$ values indicate increasing (stronger) interactions between polymer and filler. Values of $\chi'_{23}$ were influenced by type of the modifier, its amount (Fig. 5) and also by the temperature of IGC experiment. Increase of amount of the modifier decreased interactions between components of the composition. The same effect was observed for increasing temperature of IGC experiment.

The analysis of the presented experimental data leads to the following conclusions: (1) almost all examined materials are characterized by negative values of the $\chi^{\infty}_{12}$ parameter; (2) negative values of Flory–Huggins interaction parameter $\chi'_{23}$ are found for examined mixtures, what indicate strong interactions of the used components: polymer and filler. It has been found that $\chi'_{23}$ values depend on the test solute used in IGC experiments. The temperature dependence of measured parameters could be used for the prediction of the interactions of the components in polymer–filler system at technologically important conditions (temperature).



Fig. 4. Change of $\chi'_{23}$ values of chloroform for different fillers and temperatures.

## 4. Nomenclature

*Subscripts*

| | |
|---|---|
| 1 | solute |
| 2 | polymer |
| 3 | filler |
| m | mixture of polymer and filler |

*Symbols*

| | |
|---|---|
| $B_{11}$ | second virial coefficient of the solute |
| $\varphi_i$ | volume fraction of component $i$ |
| $j$ | James–Martin coefficient |
| $M_1$ | molecular mass of the solute |
| $p^{\circ}_1$ | saturated vapor pressure of the solute |
| $\rho_i$ | density |
| $R$ | gas constant |
| $V_{g,i}$ | specific retention volumes for the measured materials |
| $V^{\circ}_i$ | molar volume |
| $v_i$ | specific volume of component $i$ |
| $W_i$ | mass fraction of component $i$ |

## Acknowledgements

## References

[1] O. Smidsrod, J.E. Guillet, Macromolecules 2 (1969) 272.

[2] D.D. Deshpande, D. Patterson, H.P. Schreiber, C.S. Su, Macromolecules 7 (1974) 530.

[3] F. Dieckmann, D. Pospiech, P. Uhlmann, F. Bohme, H.R. Kricheldorf, Polymer 40 (1999) 983.

[4] A.T. James, A.J.P. Martin, Biochem. J. 50 (1952) 679.

[5] J.M. Barrales-Rienda, J. Vidal Gancedo, Macromolecules 21 (1988) 220.

[6] A. Voelkel, J. Fall, Chromatographia 44 (1997) 197.

[7] A. Voelkel, J. Fall, Chromatographia 41 (1995) 414.

[8] J. Fall, K. Milczewska, A. Voelkel, J. Mater. Chem. 11 (2001) 1042.

[9] D.R. Lloyd, T.C. Ward, H.P. Schreiber, Inverse Gas Chromatography. Characterization of Polymer and Other Materials, ACS Symposium Series No. 391, American Chemical Society, Washington, DC, 1989, 121 pp.

[10] Z.Y. Al-Saigh, P. Munk, Macromolecules 17 (1984) 803.

[11] B. Li (P. Choi), Rubber Chem. Technol. 69 (1996) 347.

[12] Z.Y. Al-Saigh, TRIP 5 (1997) 97.

[13] E. Fernandez-Sanchez, A. Fernandez-Torres, J.A. Garcia-Dominguez, J.M. Santiuste, E. Pertierra-Rimada, J. Chromatogr. 457 (1988) 55.

[14] L. Zhao, P. Choi, Polymer 42 (2001) 1075.