Characterization of the interactions in polymer/silica systems by inverse gas chromatography

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SUMMARY: Authors propose to express the magnitude of modified filler/polymer interactions by Flory – Huggins χ'_{23} parameter. We investigated polyether-urethane/modified silica systems containing different amounts of filler (5, 10, 20 % wt).
   Moreover, information on the physicochemical properties of oligomer and modified silicas were presented with the use of the following parameters:
- solubility parameter δ_2, describing properties of the polymer layer;
- Flory-Huggins parameter χ^{∞}_{12} which describes polymer-solute or mixture polymer/silica-solute interactions.

These parameters δ_2 and χ^{∞}_{12} are obtained from Inverse Gas Chromatography experiments.
The influence of the IGC experiment temperature, the content of modified silica, the nature of test solute on the evaluated parameters are presented and discussed.

Introduction

   The inverse gas chromatography is presented as a method of characterization of interactions in polymer - modified silica systems. The term *inverse* indicates that the examined material (filled polymer) is placed in a chromatographic column and studied using test solutes. Carefully selected test solutes are injected into the flow of carrier gas and transported over the surface of material. The retention time influenced by interactions between solute and stationary phase are used to estimate their interactions[1,5,6]. Thermodynamic studies of solute interactions with different types of surfaces have been examined and Flory-Huggins interaction parameter (χ^{∞}_{12}), solubility parameter (δ_1) were derived from the retention data. The magnitude of modified filler/polymer interactions has been expressed by Flory-Huggins (χ'_{23}) parameter[2,5,6].

Theory of Interactions

The retention of the test solutes is expressed by corrected retention time[3] (t_R'):

$$t_R' = t_R - t_M \tag{1}$$

For physicochemical calculations retention data are often presented with the use of specific retention volume[2,4] V_g:

$$V_g = t_R' * \frac{273.15 * F}{w_L * T} * \frac{3}{2} * \frac{\left(\frac{P_i}{P_0}\right)^2 - 1}{\left(\frac{P_i}{P_0}\right)^3 - 1} \tag{2}$$

To calculate the interactions parameter χ_{12}^∞ of polymer solute systems, V_g from equation (2) is utilized as follows:

$$\chi_{12}^\infty = \ln\left(\frac{273.15 * R}{p_1^o * V_g * M_1}\right) - \frac{p_1^o}{R * T} * (B_{11} - V_1^o) + \ln\left(\frac{\rho_1}{\rho_2}\right) - \left(1 - \frac{V_1^o}{V_2^o}\right) \tag{3}$$

When a filled polymer is used as a stationary phase in a chromatographic column, subscripts 2 and 3 are used to represent the polymer and filler, respectively. The interactions between filler and polymer are expressed in term of χ_{23}' as an indicator of miscibility of two components of the system[6]. So the χ_{23}' parameter can be derived from[3]:

$$\chi_{23}' = \frac{1}{\Phi_2 \cdot \Phi_3} \cdot \left[\ln\frac{V_{g,m}^o}{W_2 \cdot v_2 + W_3 \cdot v_3} - \Phi_2 \cdot \ln\frac{V_{g,2}^o}{v_2} - \Phi_3 \cdot \ln\frac{V_{g,3}^o}{v_3}\right] \tag{4}$$

The solubility parameter is defined as the square root of the cohesive energy density and for the volatile substances the solubility parameter may be calculated as follows[5]:

$$\delta_1 = \sqrt{\frac{\Delta H_v - RT}{V_1^o}} \tag{5}$$

For polymers having very low vapor pressures, the solubility parameter is obtained from equation:

$$\frac{\delta_1^2}{RT} - \frac{\chi_{12}^\infty}{V_1^\circ} = \frac{2\delta_2}{RT}\delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi_s^\infty}{V_1^\circ}\right) \tag{6}$$

i.e. by Guillet method. Plotting the left-hand side of equation (6) vs. δ_1 one obtains a straight-line slope proportional to δ_2 of the polymer[1,6].

Experimental

We used commercial gas chromatograph equipped with Flame Ionization Detector in the IGC experiments. Packed glass columns, 100 cm long by 0.4 mm I.D. Polymer and silica (modified silica) filled polymer were coated from solution onto Chromosorb P AW (60-80 Mesh) at approximately 15wt% loading. We also tested columns packed only by silica and modified silicas (60-80 Mesh). Columns were conditioned under helium at maximum analysis temperature over night before use.

The probe description: I, II, III, IV, V denotes amount of the octylsilane modifier in the filler: 1, 2, 3, 5, 10 wt part/100 wt parts of silica, respectively. We investigated systems containing 5, 10, 20 wt% of filler.

As a polymer we used oligomeric polyether-urethane at average molecular weight ~ 4200, having the following formula:

$$HO-(CH_2-\underset{CH_3}{CH}-O)_n-\underset{O}{C}-\underset{H}{N}-\bigcirc-\underset{H}{N}-\underset{O}{C}-(O-\underset{CH_3}{CH}-CH_2)_n-OH$$
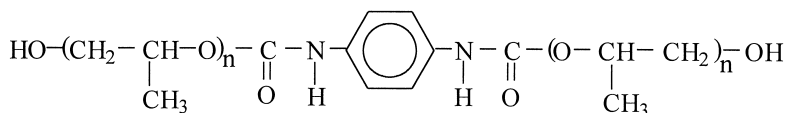
Silicas used as fillers base were precipitated and modified by A. Krysztafkiewicz and T. Jesionowski from Poznan University of Technology. These were as follows:

SiO_2 – non-modified silica – precipitated silica;

B5 – the same silica modified with octylsilane - trade name: U222 (UNISIL, Poland).

Various chemical compounds were used as the test solutes in IGC experiments. Small volumes (0.5μL) of vapor of the probes were injected manually achieve the infinite dilution conditions.

The dead time was calculated by Grobler-Balizs procedure[7].

The following compounds were used as test solutes: Pentane, Hexane, Heptane, Octane, Nonane, Decane, Methylene Chloride, Chloroform, Carbon Tetrachloride, 1,2-Dichloroethane, Diethyl Ether.

Results and Discussion

Polymer solubility parameters δ_i

As shown in Table 1 the values of δ_2 evaluated from the Guillet plot for pure components (silica and polymer) are always lower than those found for filled polymers. This fact is in accordance with our expectations as δ_2 is proportional to cohesive energy of examined material.

Table 1. Polymer and filled polymer solubility parameter δ_2 [$10^3(J/m^3)^{1/2}$].

T [K]	Polymer	Polymer+filler 5%	Polymer+filler 10%	Polymer+filler 20%	Silica (filler)	Code for filler
363	16.9±0.10	18.7±0.11	18.6±0.06	18.4±0.21	15.8±0.13	
383	15.8±0.06	18.4±0.11	18.5±0.16	18.6±0.05	13.5±0.11	SiO$_2$
403	14.6±0.16	16.6±0.02	16.6±0.10	17.2±0.10	12.4±0.15	
363	16.9±0.10	18.8±0.04	18.7±0.13	18.6±0.10	14.3±0.14	
383	15.8±0.06	18.4±0.02	18.4±0.02	17.8±0.04	14.0±0.15	IB5
403	14.6±0.16	16.9±0.02	16.4±0.06	16.6±0.11	12.9±0.22	
363	16.9±0.10	18.8±0.05	18.5±0.02	18.1±0.03	16.6±0.15	
383	15.8±0.06	18.0±0.06	18.0±0.15	17.8±0.28	14.2±0.20	IIB5
403	14.6±0.16	16.7±0.09	16.8±0.18	16.6±0.15	12.9±0.16	
363	16.9±0.10	18.7±0.04	18.2±0.13	18.1±0.06	15.1±0.21	
383	15.8±0.06	18.2±0.03	18.4±0.10	17.9±0.16	14.0±0.19	IIIB5
403	14.6±0.16	16.7±0.02	16.9±0.09	16.2±0.03	12.9±0.29	
363	16.9±0.10	18.6±0.07	18.6±0.21	18.5±0.62	15.7±0.14	
383	15.8±0.06	18.3±0.02	18.2±0.07	17.7±0.18	14.2±0.11	IVB5
403	14.6±0.16	17.1±0.03	17.0±0.06	16.5±0.10	12.9±0.11	
363	16.9±0.10	18.7±0.09	18.3±0.04	18.1±0.18	14.9±0.29	
383	15.8±0.06	18.6±0.08	18.7±0.07	17.7±0.06	13.1±0.29	VB5
403	14.6±0.16	17.0±0.07	16.9±0.03	16.5±0.06	12.3±0.23	

The increase of the δ_2 values was found for all polymer/filler systems in comparsion to the corresponding values for both components, i.e. polymer and filler. This change may be attributed to the interactions between the components of filled polymer.

The increase of the amount of the filler in the system caused most often the decrease of δ_2 value. However, the observed relationships are not linear and in several cases slight increase of δ_2 values was also observed (e.g. polymer/silica at 403K).

Increasing coverage of the silica surface (the increasing amount of octylsilane) does not cause the monotonic change of the determined parameter.

The values of δ_2 slightly decrease with increasing amount of the modifier, all systems at 363K. However, at 403K the increase of octylsilane amount lead to the increase of δ_2 value for polymer/5% filler and polymer/10% filler systems.

Increasing temperature at IGC experiments cause the decrease of the estimated δ_2 values.

Flory-Huggins interaction parameter χ_{12}^{∞}

χ_{12}^{∞} parameter is a measure of the free energy of interaction between the probe and the polymer. This parameter exhibit high values when the probes are poor solvents for the tested polymer, while low values reflect good solubility capacities. The solute/polymer interaction parameter decreases with temperature for those systems that exhibit an upper critical solution temperature. The influence of type of filler (amount of modifier) and its content is presented in Figures 1 – 4.
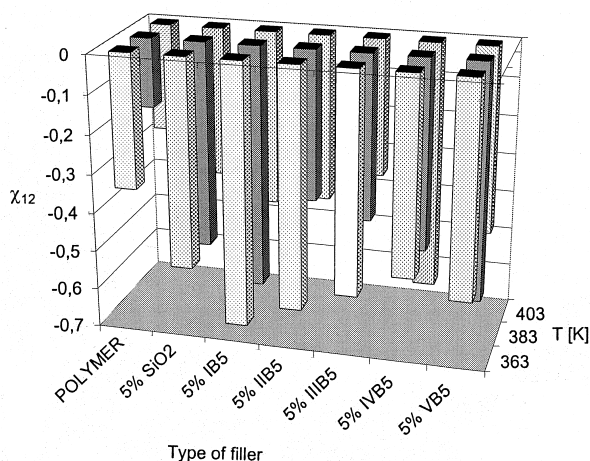

Fig. 1. Dependence of the polymer–chloroform interaction parameter χ_{12}^{∞} on the type of filler for the filled polymers at different temperatures (5% of filler)

For the pure fillers SiO_2 and IVB5 the values of χ_{12}^{∞} are above 0 (Figures 3 and 4). The filler addition in the polymer has a positive influence leading to the decrease of the χ_{12}^{∞} value.

The values of χ_{12}^{∞} for systems filled with 5% of any filler are always lower than those found for polymer.

The increasing amount of filler leads to higher proportions of silica (other filler) particles at the interface and cause the increase of χ_{12}^{∞} value.
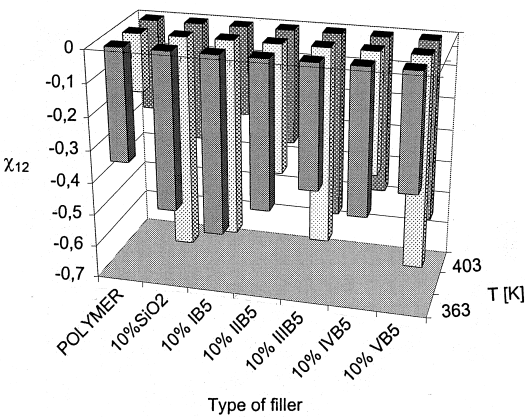
Fig. 2. Dependence of the polymer–chloroform interaction parameter χ_{12}^{∞} on the type of silica for the filled polymers at different temperatures (10% of filler).
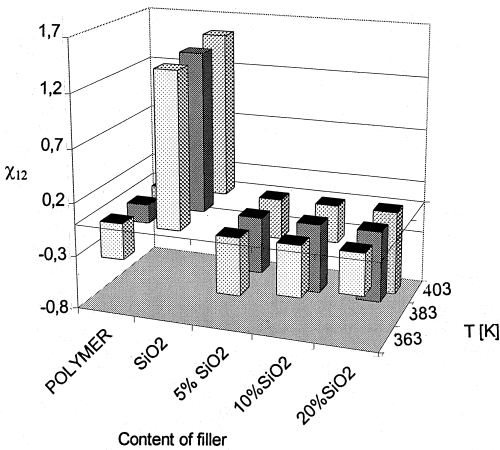
Fig. 3. Dependence of the polymer–chloroform interaction parameter χ_{12}^{∞} on the content of filler for the filled polymers at different temperatures (filler: non-modified silica).
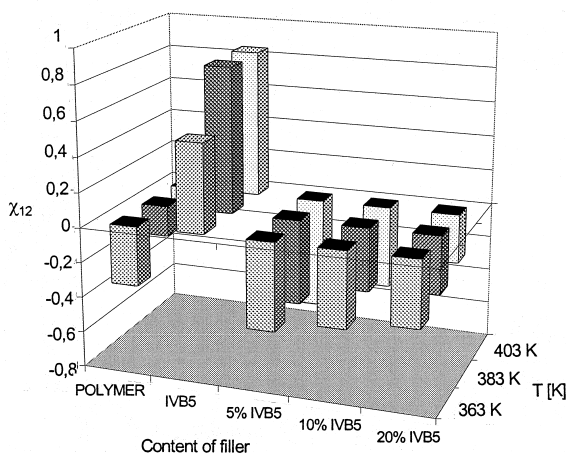
Fig. 4. Dependence of the polymer–chloroform interaction parameter χ_{12}^{∞} on the content of filler in the filled polymers at different temperatures (filler: silica modified with 5 wt % octylsilane).

Polymer - filler interaction parameter χ_{23}'

      The polymer - filler interaction parameters χ_{23}' are presented in Tables 2-3 for the three compositions examined at temperature 363 K.

Table 2. Dependence of the χ_{23}' parameter on the content of filler (SiO_2 as a filler).

	χ_{23}'		
Test solute	5%SiO_2	10%SiO_2	20%SiO_2
Pentane	-1.300±0,393	-0.952±0,049	-1.632±0,545
Hexane	-1.382±0,944	-2.337±0,707	-2.752±0,571
Heptane	-1.433±0,628	-2.082±0,190	-2.979±0,046
Octane	-1.534±0,775	-2.348±0,393	-3.165±0,700
Nonane	-1.312±0,468	-1.971±0,723	-2.953±0,960
Methylene chloride	-0.817±0,405	-1.032±0,270	-1.999±0,525
Chloroform	-0.328±0,009	-0.936±0,751	-1.891±0,369
Carbon Tetrachloride	-0.320±0,104	-0.811±0,271	-1.548±0,094
1,2-Dichloroethane	-2.031±0,985	-2.863±0,872	-3.381±0,493

The polymer/filler interaction parameter χ'_{23} may be considered on the three aspects:

° *on the type of filler* – values of this parameter were negative and independent on the type of filler. These were similar for silica/polymer (Table 2) and modified silica/polymer (Table 3) systems.

Table 3. Dependence of the χ'_{23} parameter on the content of filler (IIB5 as a filler).

Test solute	χ'_{23}		
	5%IIB5	10%IIB5	20%IIB5
Pentane	-1.029±0,077	-1.543±0,656	-3.644±0,665
Hexane	-1.325±0,683	-2.127±0,656	-4.308±0,539
Heptane	-1.652±0,722	-2.753±0,760	-4.913±0,891
Octane	-1.550±0,851	-2.972±0,039	-4.932±0,589
Nonane	-1.630±0,010	-3.151±0,406	-5.215±0,792
Methylene chloride	-0.729±0,629	-2.094±0,941	-3.874±0,871
Chloroform	-0.305±0,425	-2.051±0,576	-4.333±0,173
Carbon Tetrachloride	-0.516±0,741	-2.569±0,588	-4.411±0,238
1,2-Dichloroethane	-2.910±0,972	-3.669±0,070	-5.616±0,351

° *on the amount of filler* – the decrease in χ'_{23} (1,2-dichloroethane) values with increasing amount of filler is much higher for IIB5 than for SiO_2 filler. It could be the additional indication for a better mixing of IIB5 with the polymer due to the alkyl chains grafted onto silica. The amount of octylsilane in the filler is presented in Fig. 5.
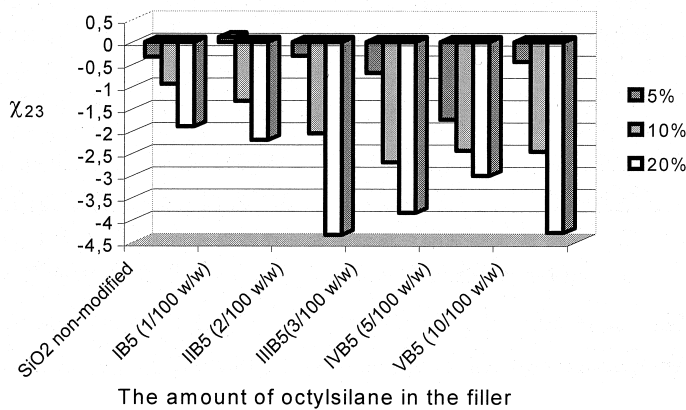

The amount of octylsilane in the filler

Fig. 5. Dependence of χ'_{23} (chloroform) parameter on the amount of modifier in filler at 363K.

°   *on the test solute* – test solutes influences the examined parameter. All χ'_{23} values were negative and the lowest ones were found for 1,2-dichloroethane.

Conclusions

The following conclusions were drawn from the experiments conducted in this work:

♦ The solubility parameters characterizing the modifier layer on the filler surface were successfully determined by IGC method.

♦ For all systems negative χ'_{23} parameters were found, indicating their thermodynamic compatibility. The χ'_{23} parameter is clearly dependent on the amount of filler in the examined systems.

♦   For that reasons we can say that the IGC method may be successfully used for characterization of polymer/filler systems.

Acknowledgment

Nomenclature Section

Subscripts:

1 – denotes solute,

2 – denotes polymer,

3 – denotes filler,

m – mixture of polymer and filler.

Symbols:

t_R – is the measured retention time [sec],

t_M – is the death time [sec],

V_g – specific retention volume (at the column temperature per gram of stationary phase),

F – is the flow rate of carrier gas [cm^3/sec], measured at room temperature,

T – temperature of experiments [K],

w_L – is the mass of the stationary phase [g],

P_i – is the inlet pressure,

P_0 – is the outlet pressure,

M_1 – is the molecular weight of the solute [g/mol],

p_1^o – is the saturated vapor pressure of the solute,

B_{11} – is the second virial coefficient of the solute,

V_1^o – is the molar volume,

ρ_i – is the density,

$V_{g,i}^o$ – are specific retention volumes for the measured materials,

v_i – is the specific volume of component i,

W_i – is the mass fraction of component i,

Φ_i – is the volume fraction of component i,

ΔH_v – is the molar enthalpy of vaporization of substance at the temperature T.

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