The Use of Flory-Huggins Parameters to Characterization of Polymer/Filler Interactions

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Summary: Any quantitative information on the strength of interactions between inorganic filler and polymer is substantial for the future application of the composite. The magnitude of adhesion of two phases may be deduced from results collected by various experimental techniques. Inverse gas chromatography is very simple and precise method.
Authors propose to express the magnitude of modified filler/polymer interactions by Flory – Huggins χ_{23} parameter. We investigated polyether-urethane/3-mercaptopropyltrimethoxysilane systems containing different amount of filler (5, 10, 20 wt %).
Moreover, information on the physico-chemical status of oligomer and modified silicas were presented with the use of the following parameters:

- solubility parameter δ_2 and its components describing properties of the polymer layer;
- Flory-Huggins parameter χ_{12} which describes polymer-solute or filled polymer-solute interactions.

Subscripts *1*, *2*, *3* and *m* refers to solute, polymer, filler and polymer/filler mixture, respectively. Pure, low molecular weight, volatile test solutes were selected and injected into a chromatographic column.
The influence of the IGC experiment, temperature, the content of modified silica and the nature of test solute on the evaluated parameters are presented and discussed.

Introduction

Presently, it is well established that introduction of a filler into polymer leads to the changes in thermodynamic interaction parameter between components χ_{23}. Depending on the nature of interaction between polymeric components and filler surface may either increase or decrease. The introduction of a filler influences significantly states of dispersion of nanoparticles.

Changes in χ_{23} were explained by the specific interactions of the polymer with the filler surface. The model of interaction between mixture components has been proposed, according to which the total interaction parameter can be described as[1]:

$$\chi_{23} = \frac{1}{\phi_2 * \phi_3} * \left(\ln \frac{V_{g,m}}{W_2 * v_2 + W_3 * v_3} - \phi_2 * \ln \frac{V_{g,2}}{v_2} - \phi_3 * \ln \frac{V_{g,3}}{v_3} \right) \quad (1)$$

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where: subscript *1* denotes the solute, *2* denotes the polymer, *3* denotes filler and *m* denotes mixture polymer/filler; φ_2, φ_3 are the volume fractions of polymer and filler, respectively; V_g is the specific retention volume of the test solute.

The values of χ_{12} may be calculated from the equation presented earlier[1, 2]. χ_{12} and χ_{23} parameters have been used to evaluate the properties of different systems[3, 4].

The aim of the present work is to express the magnitude of modified filler/polymer interactions by Flory-Huggins χ_{23} parameter. It may be deduced from results collected in Inverse Gas Chromatographic (IGC) experiment. We have also tried to explain the influence of the temperature and the content of modified silica on the evaluated parameters. Information on physicochemical status of examined materials was presented with the use of the following parameters:

- solubility parameter δ_2 and its components, describing properties of the polymer layer[5, 6],
- Flory-Huggins χ_{12} parameter, which describes polymer-solute interactions[7].

Experimental

The IGC experiments were carried out with the use of oligomeric polyether-urethane (average molar mass ~ 4200 g·mol^{-1}) filled with modified (with 3-mercaptopropyl-trimethoxysilane) silica (B4) systems. Precipitated and modified silica used as a filler was characterized by: specific surface area S=160 m^2·g^{-1}, size of primary particles about 40 nm and mean diameter of agglomerates about 900 nm. We investigated systems containing 5, 10 and 20% of filler. The probes description IB4, IIB4, IIIB4, IVB4, VB4 denotes the amount of the modifier in the filler: 1, 2, 3, 5, 10 wt. part/100 wt. parts of silica, respectively.

Various chemical compounds were used as the test solutes in IGC experiments. Small volumes (0.5μL) of the probes were injected manually to achieve the infinite dilution conditions of the probes. The dead time was calculated by Grobler-Balizs procedure[8]. The following compounds were used as test solutes: Pentane, Hexane, Heptane, Octane, Nonane, Decane, Methylene Chloride, Chloroform, Carbon Tetrachloride, 1,2-Dichloroethane and Diethyl Ether.

Results and Discussion

Flory-Huggins' interaction parameter χ_{12} is a measure of free energy of interactions between the probe and the examined material (polymer, filler or filled polymer). The influence of the content of filler and amount of modifier in the filler were presented in Figures 1 - 2.

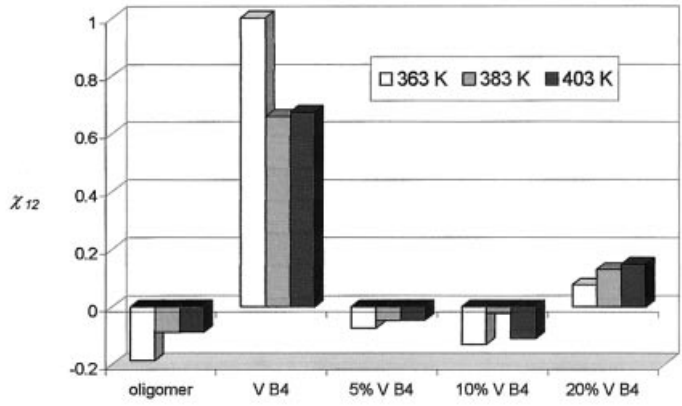

Figure 1. Dependence of the polymer–dichloromethane interaction parameter χ_{12} on the content of filler at different temperatures.

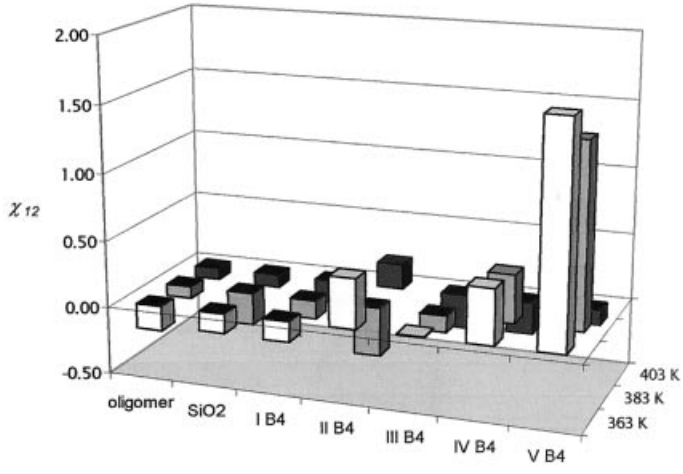

Figure 2. The influence of the amount of the modifier on the filler on χ_{12} parameter at different temperatures (dichloromethane as the test solute).

Flory-Huggins' interaction parameter χ_{23} expresses the magnitude of filler/polymer interactions in investigated systems. The dependence of χ_{23} on the content of the filler is presented in Table 1.

Table 1. Flory-Huggins' χ_{23} parameter at 383K.

chloroform	5%	10%	20%
IB4	-3.6067	-1.4946	-1.1947
IIB4	-2.5592	-1.3628	-0.6340
IIIB4	-1.6863	0.8709	-2.1791
IVB4	-1.9702	-2.7567	-1.2400
VB4	-1.5176	-1.0512	-1.3474

Negative values of χ_{23} parameter were most often found for our systems, indicating the thermodynamic compatibility between the modified filler and the polymer medium. The best results were obtained for IB4 and IIB4 systems, i.e. the highest compatibility is achieved for the filler modified with very limited amount of the modifier (1 and 2 wt. parts). The increase of the amount of the filler caused the increase of χ_{23} values indicating worse mixing of components. The influence of the test solutes on the values of this parameter is presented in Figure 3. Dependence of the amount of the modifier in the filler is presented in Figure 4.

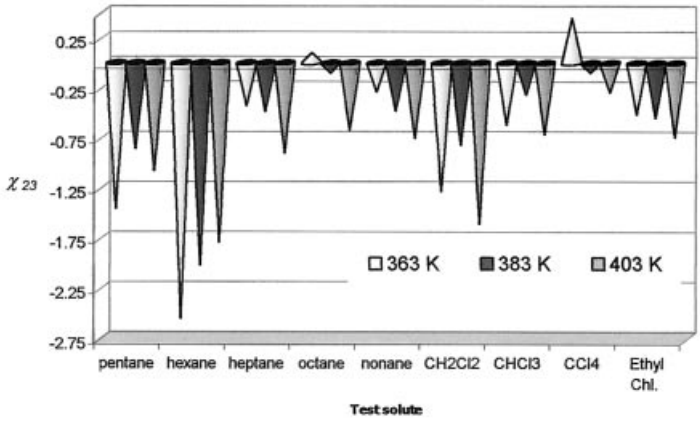

Figure 3. The influence of the test solutes on the values of χ_{23} parameter for 20% IB4 system.

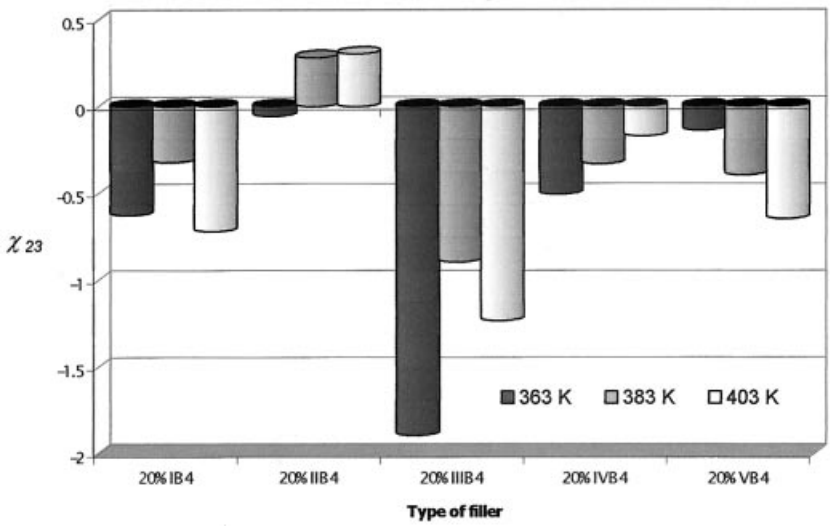

Figure 4. The influence of the type of filler on the values of χ_{23} parameter (chloroform as the test solute).

These observed effects indicate that probably exist "required" state of the filler surface at which the system achieves highest stability. Modification of silica surface with 3-mercaptopropyltrimethoxysilane causes hydrophobization of the surface. Too deep hydrophobization with 3 and more wt. parts leads to decrease of the system stability.
The addition of hydrophobized silica to relatively polar polymer produces stable mixtures only for small amount of the filler. The higher amounts of the filler cannot be stabilized efficiently. We like to call this effect – the *stabilization capacity*.

The values of solubility parameter δ_2 and its components evaluated from Guillet' plot are given in Table 2.

Table 2. Solubility parameter δ_2 [MPa$^{1/2}$].

10% IV B4	363 K	383 K	403 K
δ_d	10.69	9.46	9.96
δ_p	7.33	15.88	19.77
δ_2	17.46	16.46	16.76

The decrease of δ_2 is caused by the interactions between the components of filled polymer.

Conclusion

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

1. The IGC method can be used for the characterization of interactions in polymer/filler systems.

2. We obtained the negative values of χ'_{23} parameter indicating strong interactions between components.

3. An addition of the filler to polymer enhances the interactions between the test solutes and examined compositions.

4. Solubility parameter and its components are useful in the prediction of compatibility of polymers with fillers.

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Nomenclature Section

Subscripts:

1 – denotes solute,

2 – denotes polymer,

3 – denotes filler,

m – mixture of polymer and filler.

Symbols:

ϕ_i – is the volume fraction of component *i*,

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

W_i – is the mass fraction of component *i*,

v_i – is the specific volume of component *i*.

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