

Interactions in PEG/Aerosil® and PLA/Aerosil® composites described by *IGC*-determined Flory-Huggins χ_{23} parameter

Kasylda Milczewska · Adam Voelkel · Katarzyna Piędzia

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Abstract The magnitude of the interactions between two phases may be deduced from results collected by various experimental techniques. One of them is Inverse Gas Chromatography (*IGC*). *IGC* is an extension of conventional gas chromatography in which a non-volatile material to be investigated is immobilized on a column. Parameters determined during *IGC* experiments may be successfully used in the characterization of polymers and their blends, composites and fillers as well as other materials, quantification of the interactions between the components of a polymer's mixture including the interactions between polymeric components and filler surface. Authors propose to express the magnitude of filler–polymer interactions by using the modified procedure of the determination of Flory–Huggins χ_{23} parameter. It was calculated from retention data of test solutes collected during inverse gas chromatographic experiments. Here, this method was applied for characterization of a series of poly(ethylene glycol) 10,000 (PEG) and poly(L-lactide) (PLA) (59,000) compositions with Aerosil® 200 V (AR_200). The usefulness of some methods to eliminate dependence of χ_{23} on the type of test solute was examined and discussed.

Keywords *IGC* · Flory-Huggins parameter · Polymer–filler interaction

Introduction

Polymer blends are a new class of materials needed to replace heavy metal alloys. Blending of polymers is a fast and inexpensive route to obtaining this class of materials [1].

Composite materials (polymers with inorganic fillers) play an important role in many fields of science. Addition of filler lowers the cost and also improves the tensile strength of the base resin. The strength of the interactions between components of the composite is the key factor in polymer materials characterization. Filler content, chemical characteristics of the components, and filler characteristics significantly influence the rheological and mechanical properties of the polymer composites. Also any change in the polymer–filler interactions affects the properties of the composition.

A variety of experiments are being used to determine material compatibility. Only a few techniques can give quantitative information about the change of free energy when mixing two components. One of them is inverse gas chromatography [2]. During the years this technique has become an accurate, reliable, and fast method for physicochemical characterization of polymer systems. The properties of the examined material are deduced from the retention data of test solutes of different chemical natures. Retention parameters depend on the magnitude of interactions between test solutes and examined material, e.g. a polymer blend playing the role of the stationary phase in a chromatographic column. Retention data are further used for calculation of physicochemical characteristics of various materials.

The usefulness of *IGC* for determining polymer–small molecule interactions is well established. Experimentally determined retention parameters are easily recalculated into Flory–Huggins parameters, using the equation [3]:

$$\chi_{12(3)}^{\infty} = \ln \left(\frac{273.15 \cdot R}{p_1^o \cdot V_g \cdot M_1} \right) - \frac{p_1^o}{R \cdot T} \cdot (B_{11} - V_1) + \ln \left(\frac{\rho_1}{\rho_{2(3)}} \right) - \left(1 - \frac{V_1}{V_{2(3)}} \right) \quad (1)$$

K. Milczewska (✉) · A. Voelkel · K. Piędzia
Poznan University of Technology, Institute of Chemical Technology
and Engineering, Pl. M. Skłodowskiej-Curie 2, 60-965 Poznań,
Poland
e-mail: Kasylda.Milczewska@put.poznan.pl

where: 1 denotes the solute, and 2 or 3 denotes the examined material (polymer or filler, accordingly). M_1 is the molecular weight of the solute; p_1^o is the saturated vapour pressure of the solute, and B_{11} is the second virial coefficient of the solute. V_i is the molar volume; ρ_i is the density. R is the gas constant, and V_g is the specific retention volume.

In the case of the mixture (e.g. polymer–filler composition) Eq. (1) could be rearranged into [4, 5]:

$$\chi_{1m}^{\infty} = \ln\left(\frac{273.15 \cdot R}{p_1^o \cdot V_g \cdot M_1}\right) - \frac{p_1^o}{R \cdot T} \cdot (B_{11} - V_1) + \ln\left(\frac{\rho_1}{\rho m}\right) - \left(1 - \frac{V_1}{V_2}\right) \cdot \varphi_2 - \left(1 - \frac{V_1}{V_3}\right) \cdot \varphi_3 \quad (2)$$

where φ_2 and φ_3 are the volume fractions of polymer and filler, while index m means a composition.

The interaction between the two components of composition is expressed in terms of χ'_{23} calculated from [6, 7]:

$$\chi'_{23} = \frac{\chi_{23}^{\infty} \cdot V_1}{V_2} = \frac{1}{\varphi_2 \cdot \varphi_3} \cdot \left(\ln \frac{V_{g,m}}{W_2 \cdot \nu_2 + W_3 \cdot \nu_3} - \varphi_2 \cdot \ln \frac{V_{g,2}}{\nu_2} - \varphi_3 \cdot \ln \frac{V_{g,3}}{\nu_3} \right) \quad (3)$$

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

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 [8].

A large positive value indicates the absence of or negligible interactions between components; a low value indicates favourable interactions, while a negative value indicates strong interactions. Values of Flory-Huggins χ'_{23} parameter depend on the chemical structure of the solute, and it is a common phenomenon, although not allowed by the theory [9]. It has been interpreted as a result of preferential interactions of the test solute with one of two components. Deshpande et al. [10] applied this technique for the determination of thermodynamic interactions between components of a mixture of polymer and nonpolymeric compound. Su et al. [11] used this technique to measure the interaction parameter of poly(vinyl chloride) (PVC) and dioctyl phthalate as a plasticizer to study their compatibility. Later, this method was also used to measure the compatibility of polymer blends. However, many studies have shown that the polymer-polymer interaction parameters determined by this technique depend

on the probes used. Hsu and Prausnitz and Patterson and co-workers suggested that the compatibility of polymeric components in solution should reflect not only the interaction between the components themselves, that is, χ'_{23} , but also the difference in the strengths of the polymer-probe interactions, that is: $\Delta\chi = |\chi_{12} - \chi_{13}|$. They called it the $\Delta\chi$ effect, and a large $\Delta\chi$ value, in addition to a high χ'_{23} value, suggests incompatibility.

Deshpande and Farooque observed probe dependency and tried to develop a method to evaluate probe-independent interactions [12].

Milczewska and Voelkel [7] discussed some of the methods of evaluating probe-independent interaction parameters. One of the solutions may be a procedure proposed by Zhao and Choi [4, 5]. The authors proposed to use 'common reference volume' (V_o), which eliminates the problem. For the reference volume, they used molar volume of the smallest repeated unit of polymer. Their definition of χ differed from the traditional definition by the ratio of the reference volume to the probe volume (V_o/V_1). When a common reference volume was used, the data conformed to the ternary version of the Flory-Huggins lattice theory, and unique χ_{23} values were obtained.

Zhao and Choi demonstrated that by selecting a proper common reference volume for analyzing IGC data, one can yield reliable solvent-independent χ_{23} , so long as the solvents used satisfy the zero $\Delta\chi$ criterion.

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

$$\chi_{1m} = \frac{V_o}{V_1} \left(\ln \frac{273.15 \cdot R}{M_1 \cdot V_g \cdot p_1^o} - 1 + \left(1 - \frac{V_1}{V_2}\right) \cdot \varphi_2 + \left(1 - \frac{V_1}{V_3}\right) \cdot \varphi_3 - \left(\frac{B_{11} - V_1}{R \cdot T}\right) \cdot p_1^o \right) \quad (4)$$

and

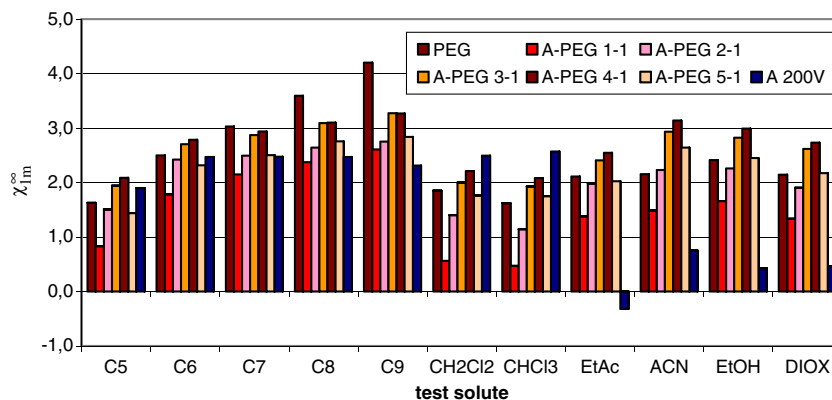
$$\chi_{1m} = \varphi_2 \cdot \chi_{12} + \varphi_3 \cdot \chi_{13} - \varphi_2 \cdot \varphi_3 \cdot \chi'_{23} \quad (5)$$

Equation (5) 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 of 1 and an intercept of $-\varphi_2 \cdot \varphi_3 \cdot \chi'_{23}$.

Table 1 Compositions and used symbols

Used symbol A-PEG/A-PLA	Aerosil—PEG Weight fractions [g]	Aerosil—PLA Weight fractions [g]
0-1	0.00 - 2.00	0.00 - 1.00
1-1	1.00 - 1.00	0.50 - 0.50
2-1	1.35 - 0.65	0.68 - 0.32
3-1	1.50 - 0.50	0.75 - 0.25
4-1	1.60 - 0.40	0.80 - 0.20
5-1	1.66 - 0.34	0.88 - 0.12

Fig. 1 Values of χ_{1m}^∞ parameter for compositions with PEG at 353 K



J. C. Huang [13] and R. Deanin [14] rearranged Eq. (5) into the following form:

$$\frac{\chi_{1m}}{V_1} = \frac{\varphi_2 \cdot \chi_{12} + \varphi_3 \cdot \chi_{13}}{V_1} - \frac{\varphi_2 \cdot \varphi_3 \cdot \chi'_{23}}{V_2} \quad (6)$$

The polymer-polymer interaction term can be determined from the intercept at $\left(\frac{\varphi_2 \cdot \chi_{12} + \varphi_3 \cdot \chi_{13}}{V_1}\right) = 0$. This modification provided smaller standard deviations for the slope and the polymer-polymer interaction parameter [15]. J. C. Huang [16] presented some of the constraints of the models used. He noticed that the IGC technique couldn't be used in immiscible systems, because the equation of the parameter was derived based on the assumption of miscible components (blends). However, two different monomers can be brought together into a one-component system by copolymerization. So the interaction parameters between solutes and copolymers should follow a trend intermediate between the two homopolymers.

Flory-Huggins parameters from basic procedures for such types of systems were calculated successfully [17, 18].

The aim of this work was to present the possibility of applying the thermodynamic relations determined by IGC

for polymer blends to polymer-inorganic filler mixtures. The authors proposed to use Zhao-Choi's and Huang's procedures to determine interaction parameters in polymer-filler systems.

Materials

IGC experiments were used to examine the interactions of polymer-filler systems containing poly(ethylene glycol) (PEG) (average molar mass $\sim 10,000 \text{ g}\cdot\text{mol}^{-1}$) and poly(L-lactide) (PLA) ($55,000 \text{ g}\cdot\text{mol}^{-1}$). Polymers (supplied from Sigma Aldrich) were mixed with hydrophilic fumed silica – Aerosil®200 V (A) [19] (delivered from Evonik Industries). Detailed compositions of tested formulations are shown in Table 1.

Experimental conditions

Measurements were carried out with the use of Chrom5 (Kovo, Czech. Rep.) gas chromatograph equipped with FID. Teflon columns, $50 \text{ cm} \times 0.3 \text{ mm}$ I.D., were packed with the support coated with polymer or filled polymer. Polymers,

Fig. 2 Values of χ_{1m}^∞ parameter for compositions with PLA at 353 K

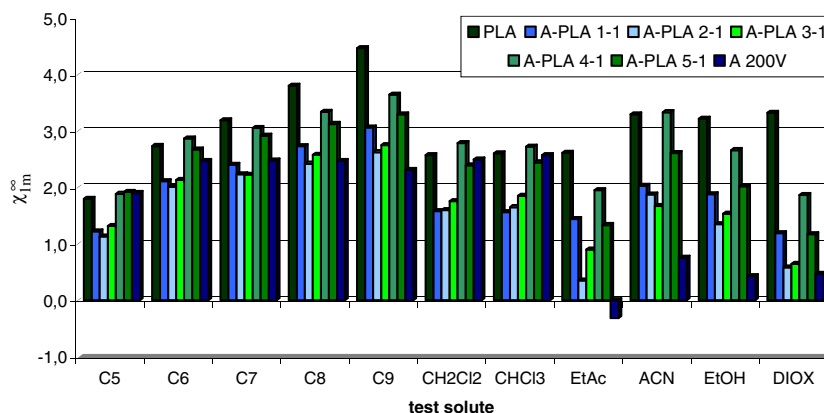
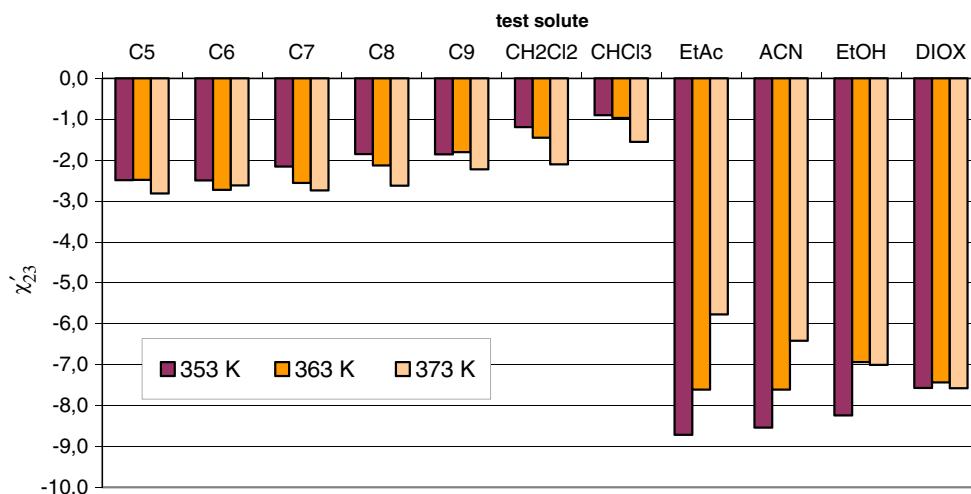


Fig. 3 Values of χ'_{23} parameter for A-PEG 4-1 composition



filler and compositions were mixed with glass beads at 1 wt% loading. The following compounds were used as test solutes: pentane (C5), hexane (C6), heptane (C7), octane (C8), nonane (C9), methylene chloride (CH₂Cl₂), chloroform (CHCl₃), ethyl acetate (EtAc), acetonitrile (ACN), ethanol (EtOH), and 1,4-dioxane (DIOX). Dry helium with a flow rate of 15 ml/min was used as a carrier gas. The investigated materials were mixed homogeneously with the glass beads. Measurements were carried out at infinite dilution, which means that a very small amount of the test solutes was injected onto the chromatographic column filled with the examined material. All columns were conditioned overnight at the flow rate and temperature used later during IGC experiments. Retention parameters of test solutes (retention time and volume) were used to calculate values of physicochemical parameters characterizing the examined materials.

Results

Flory-Huggins χ_{1m}^{∞} and χ'_{23} parameters

Values of Flory-Huggins parameter χ_{1m}^{∞} were calculated from Eq. (2) for all investigated compositions. All the data are positive, but in all systems we can find solute for which the composition is slightly miscible (Figs. 1 and 2). The strongest interactions with test solute were observed for compositions A-PEG 1-1 and A-PLA 2-1. Aerosil also strongly interacts with the test solutes – significantly with ethyl acetate. Lower values than for alkanes were obtained for the polar probes. The best solvent (the strongest solvent–composition interaction) for both series of compositions is ethyl acetate.

Flory-Huggins parameter χ'_{23} indicates the magnitude of interactions between components of the composition. In compositions with PEG (Fig. 3), for almost all proportions,

Fig. 4 Values of χ'_{23} parameter for A-PLA 1-1 composition

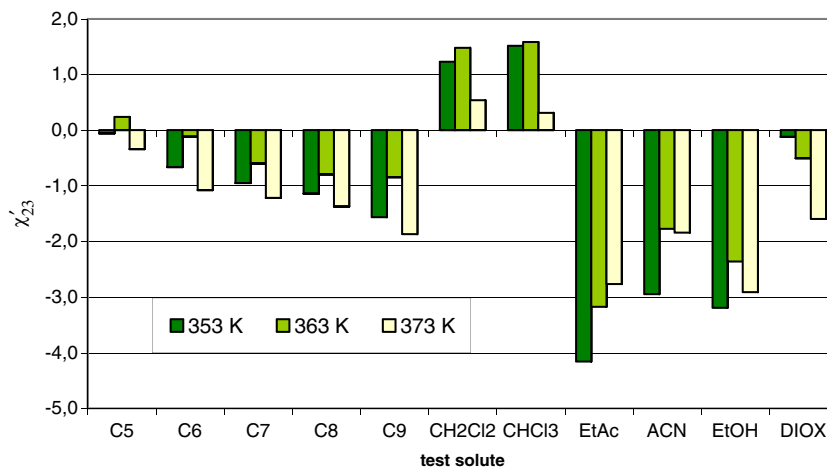


Table 2 Values of χ'_{23} calculated from Zhao-Choi procedure for PEG composites

χ_{23}^{ZC}	353 K	363 K	373 K
A-PEG 1-1	-1.26E-03	-8.25E-04	-6.28E-04
A-PEG 2-1	-8.79E-04	-3.23E-04	-1.43E-04
A-PEG 3-1	1.26E-04	1.79E-05	-3.95E-04
A-PEG 4-1	4.66E-04	9.86E-04	1.67E-03
A-PEG 5-1	-9.15E-04	-4.66E-04	3.05E-04

Correlation coefficient higher than $R^2 = 0.94$

negative values of χ'_{23} were obtained. In a series of A-PLA (Fig. 4) compositions, only the 1-1 Aerosil-PLA mixture is characterized by some negative χ'_{23} values. The lowest values of χ'_{23} are obtained for polar probes. Column temperature also influences the values of determined parameters. χ_{23} values for alkanes decreased with increasing temperature, but increased for polar probes.

Because of χ_{23} probe dependency, we used the procedures of Zhao-Choi and Huang for calculation of solute-independent χ_{23} .

Zhao-Choi procedure

For all compositions, values of the parameter χ'_{23} were calculated from the procedure of Zhao-Choi (Eq. 4 and 5). As a ‘reference volume’, we used molar volume of repeated unit of polymers (in the case of PEG, it was $V_o=55.8$ and, for PLA $V_o=74.5$ [cm³/mol]). Results are presented in the Tables 2 and 3.

Almost all χ_{23}^{ZC} values are slightly negative (with the exceptions of A-PEG 3-1 and 4-1), which may suggest the existence of strong interactions in these compositions. χ_{23}^{ZC} value increases with the increasing of the filler content in A-PEG compositions. χ_{23}^{ZC} values are smaller for A-PLA series than for A-PEG composites. The weakest interactions in A-PLA composites were found for 5-1 and 4-1; the highest

Table 3 Values of χ'_{23} calculated from Zhao-Choi procedure for PLA composites

χ_{23}^{ZC}	353 K	363 K	373 K
A-PLA 1-1	-5.24E-04	-5.91E-04	-3.90E-04
A-PLA 2-1	-8.46E-04	-8.60E-04	-6.31E-04
A-PLA 3-1	-8.06E-04	-9.13E-04	-6.45E-04
A-PLA 4-1	-2.69E-05	-4.03E-05	1.34E-05
A-PLA 5-1	-2.69E-04	-2.15E-04	7.93E-04

Correlation coefficient higher than $R^2 = 0.955$

Table 4 Values of χ'_{23} calculated from Huang procedure for PEG composites

χ_{23}^H	353 K	363 K	373 K
A-PEG 1-1	-1.88E-05	-1.41E-05	-1.17E-05
A-PEG 2-1	-2.80E-05	-2.18E-05	-1.72E-05
A-PEG 3-1	-3.32E-05	-2.59E-05	-1.17E-05
A-PEG 4-1	-4.21E-05	-3.27E-05	-2.73E-05
A-PEG 5-1	-4.89E-05	-3.95E-05	-3.34E-05

Correlation coefficient higher than $R^2 = 0.958$

value of χ_{23}^{ZC} . The strongest interactions was shown for A-PLA 3-1 composite.

Huang’s procedure

For all investigated compositions we also calculated χ'_{23} parameters from the J-C. Huang procedure (Eq. 6). The obtained values are presented in the Tables 4 and 5.

For both series of compositions we obtained negative values of the χ_{23}^H parameter. Compositions with PEG were characterized by smaller χ_{23}^H values than A-PLA. The lowest values were obtained for A-PEG 5-1 and A-PLA 5-1 compositions. In the Huang procedure, increasing the amount of the filler caused a decrease of the χ_{23}^H values.

The arrangement of the examined compositions according to the procedures proposed by Zhao-Choi and Huang is different. This is probably due to varying the volume used as ‘reference’ for calculation of χ_{1m} .

From values of χ'_{23} calculated on the base of “solute-independent” procedures, we can state that the best composition with the highest interaction between components is A-PLA 3-1 composition (the lowest value of χ_{23}^{ZC}).

From χ_{23}^H values, it follows that the strongest interaction occurred for the A-PEG 5-1 composition.

In literature Flory-Huggins interaction parameter χ_{23} is usually presented as a ratio χ_{23}/V_2 to discount the reference

Table 5 Values of χ'_{23} calculated from Huang procedure for PLA composites

χ_{23}^H	353 K	363 K	373 K
A-PLA 1-1	-5.23E-07	-4.09E-07	-2.95E-07
A-PLA 2-1	-6.59E-07	-4.55E-07	-3.86E-07
A-PLA 3-1	-2.27E-07	-4.55E-07	-3.86E-07
A-PLA 4-1	-1.45E-06	-1.09E-06	-1.30E-06
A-PLA 5-1	-1.41E-06	-1.61E-06	-4.09E-07

Correlation coefficient higher than $R^2 = 0.981$

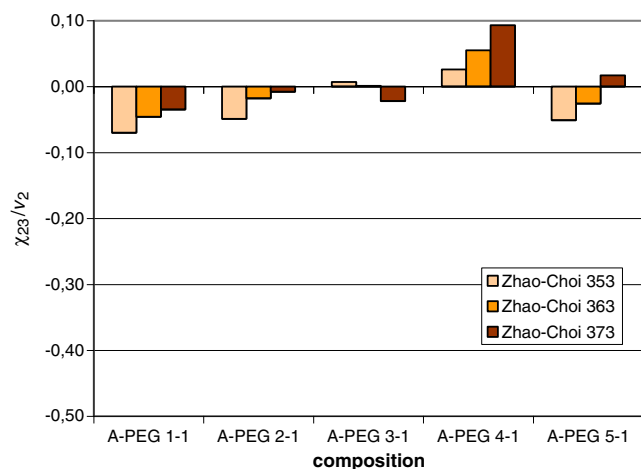


Fig. 5 Values of χ_{23}/v_2 calculated from Zhao-Choi procedure for PEG compositions

volume value. In our case, values of χ_{23}/v_2 for both procedures are presented in Figs. 5 and 6 (Zhao-Choi) or Figs. 7 and 8 (Huang).

For values obtained from the Huang procedure for both compositions, we can observe linear dependency from the amount of filler; for calculations from Zhao-Choi that dependence isn't linear.

The influence of the temperature was also observed. For A-PEG compositions an increase of the temperature causes an increase of the values of Flory-Huggins parameter χ_{23} ; whereas for A-PLA compositions the strongest interaction (the smallest χ_{23} values) were observed in the middle temperature independently from calculation procedure.

Which procedure is "better"? For those kinds of material, i.e., compositions of polymer with inorganic filler Huang's

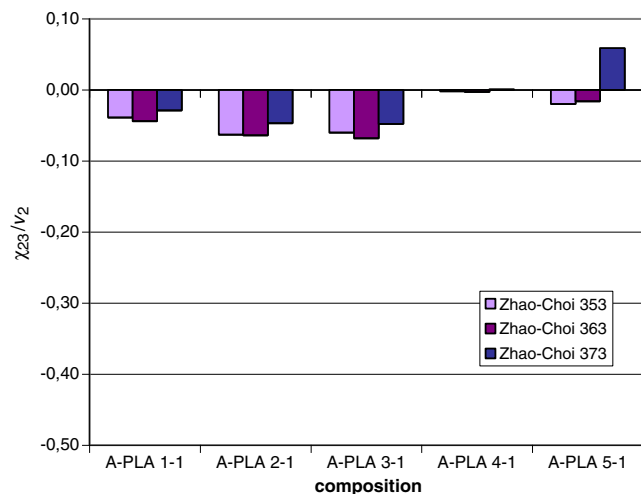


Fig. 6 Values of χ_{23}/v_2 calculated from Zhao-Choi procedure for PLA compositions

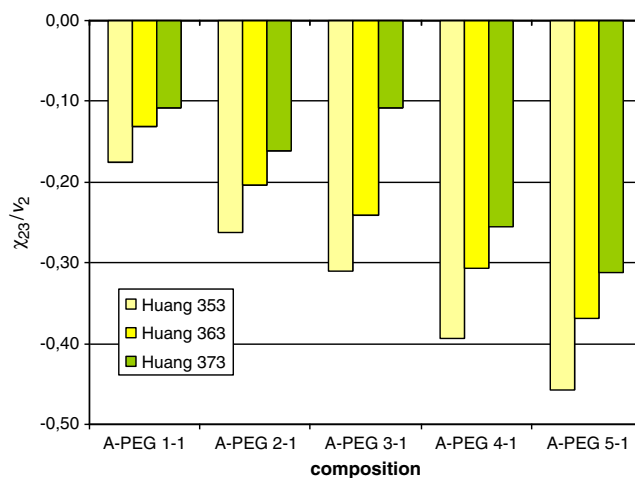


Fig. 7 Values of χ_{23}/v_2 calculated from Huang procedure for PEG compositions

method seems to be more suitable. Values of χ_{23}/v_2 calculated by the Huang method for both series of compositions are smaller than those obtained from the Zhao-Choi equation. This is more clear for interpretation of the strength of interaction (values ~ 0 may suggest existence of interaction or not). Linear dependence of χ_{23}/v_2 values on the amount of the components is an additional advantage. It may facilitate the prediction of the magnitude of interactions in future investigations. However, the existence of such relationship should be confirmed for a larger group of investigated complex materials.

Results obtained by using standard and "solute-independent" Huang's procedures indicated strong interactions between components, as negative values of χ_{23} were found. Therefore, we suggest the use of the parameters determined

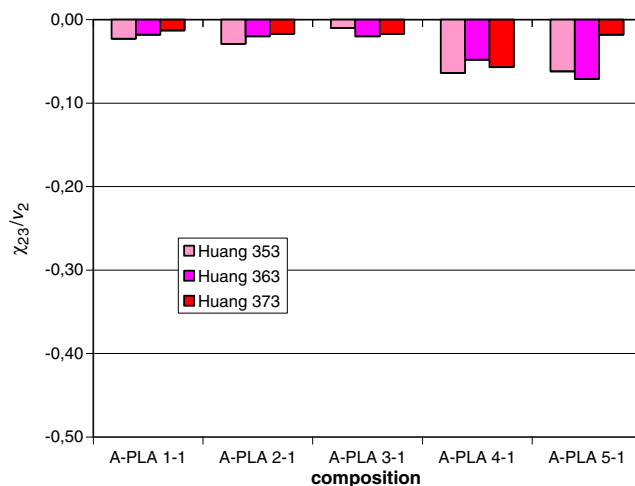


Fig. 8 Values of χ_{23}/v_2 calculated from Huang procedure for PLA compositions

by Huang's method in drawing conclusions on the properties of the examined complex polymeric systems.

Conclusion

The *IGC* method was used for estimating the magnitude of interactions between the components of polymer compositions. Flory-Huggins parameters for polymer–filler systems were calculated using standard and “solute-independent” methods. Negative values of Flory-Huggins interaction parameter χ'_{23} were found for almost all examined mixtures, which indicates significant interactions of the components used. It has been found that χ'_{23} values depend on the nature of the test solute used in the *IGC* experiment. Stronger interactions were observed for the A-PEG composition (lower values of χ'_{23}). Application of Zhao-Choi and Huang procedures leads to elimination of solute dependence of χ'_{23} . Values χ_{23}/V_2 obtained from Huang procedure for both compositions depend linearly on the amount of filler. By using χ_{23}/V_2 values, one may follow the changes in the magnitude of interactions between the components of the composition resulting from the changes of filler properties, its amount and temperature.

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