Use of Flory–Huggins Parameters in the Characterization of Polymer–Filler Compositions

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ABSTRACT: Any quantitative information on the strength of interactions between an 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. A Flory–Huggins interaction parameter (χ'_{23}) was earlier successfully used in the characterization of polymer blends. We propose to express the magnitude of modified filler/polymer interactions by using χ'_{23}. It was calculated from retention data of test solutes during an inverse gas chromatography (IGC) experiment. IGC is an extension of conventional gas chromatography in which a nonvolatile 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, fillers, and other materials and the quantification of the interactions between the components of polymer mixtures, including the interactions between polymeric components and filler surfaces. Here this method is applied to the characterization of a series of poly(ether urethane)/modified carbonate–silicate filler systems containing different amounts of a filler (5, 10, and 20 wt %). The possibilities and limitations of the IGC method are shown. The usefulness of some methods for minimizing the $\Delta\chi$ effect (the dependence of χ'_{23} on the type of test solute) is examined and discussed. J Appl Polym Sci 107: 2877–2882, 2008

Key words: inverse gas chromatography; polymer-filler interaction; compositions

INTRODUCTION

Mixtures of different types of materials, such as polymers, blends, modified fillers, and compositions, are used extensively to produce commercially useful materials having combinations of properties not normally found in a single component. Many of the properties and processing characteristics of those mixtures depend on whether they are miscible or not. The theory contains parameters related to the pure components. However, mixture parameters that characterize polymer–polymer and polymer–filler interactions are generally required as well.[1]

The Flory–Huggins interaction parameter (χ), an important factor of miscibility of polymer blends and solutions, has been determined by a number of methods and a lot of researchers.

Small-angle neutron scattering (SANS) is one of the methods widely used to obtain Flory–Huggins interaction parameters for polymer blends because of the high contrast between labeled and unlabeled spices. The scattering interaction parameter (χ_S) is different from the interaction parameter (χ_F) in the Flory–Huggins theory. That parameter can be written as the derivative form of the Flory–Huggins interaction parameter:[2]

$$2\chi_S = 2\chi_F - 2\cdot(1-2\phi)\cdot\frac{\partial\chi_F}{\partial\phi} - \phi\cdot(1-\phi)\cdot\frac{\partial^2\chi_F}{\partial\phi^2} \quad (1)$$

where ϕ is the volume fraction. χ_S is obtained by SANS. Both χ_F and χ_S are dependent on the reference volume.

In recent years, the Flory–Huggins interaction parameter has been determined with the melting point depression method for crystal-containing polymers by differential scanning calorimetry.[3] A single glass-transition temperature observed for blends suggests the miscibility of the components. Measurement of the melting temperature depression for blends allows the determination of a Flory–Huggins interaction parameter (χ_{12}^{∞}) of the two polymers in the melt with the Nishi–Wang equation.[4]

Inverse gas chromatography (IGC) is a useful method for determining polymer/small molecule interactions. This method provides a fast and convenient way of obtaining thermodynamic data for

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TABLE I
Values of χ_{12}^{∞} for the 20% N1–PU System at Different Temperatures

Test solute	363 K	373 K	383 K	393 K	403 K
C_5	0.578	0.626	0.521	0.628	0.417
C_6	0.911	0.958	0.864	0.949	0.878
C_7	0.822	0.898	0.798	0.849	0.763
C_8	0.852	0.906	0.828	0.852	0.793
C_9	0.858	0.943	0.870	0.882	0.827
CH_2Cl_2	0.047	0.157	0.150	0.170	0.195
$CHCl_3$	−0.288	−0.169	−0.164	−0.098	−0.051
CCl_4	0.351	0.414	0.371	0.397	0.406
$C_2H_2Cl_2$	0.261	0.346	0.302	0.324	0.365

concentrated polymer systems. This technique can also be used to measure polymer–polymer interaction parameters via a ternary solution approach.[5]

IGC can be applied to observe the interactions in filled polymer/organic solvent and modified filler/polymer systems under conditions approaching infinite dilution of the volatile test solute (organic solvent/probe).[6–11]

The examined material (filled polymer) is placed into a chromatographic column and investigating with carefully selected test solutes. The retention time, influenced by interactions between the test solute and stationary phase, is used to estimate their interactions. χ_{12}^{∞} (expressing the polymer/test solute interactions) is derived from the retention data [specific retention volume (V_g)] of carefully selected test solutes according to the following equation:[8,9,12–14]

$$\chi_{12}^{\infty} = \ln\left(\frac{273.15 \cdot R}{p_1^o \cdot V_g \cdot M_1}\right) - \frac{p_1^o}{R \cdot T} \cdot \left(B_{11} - V_1^o\right) - \left(1 - \frac{V_1^o}{V_2^o}\right) - 1 \qquad (2)$$

Subscript 1 denotes the solute; subscript 2 denotes the polymer; M_1 is the molecular weight; p_1^o is the saturated vapor pressure; B_{11} is the second virial coefficient; V_1^o and V_2^o are the molar volumes of the test solute and polymer, respectively; ρ_i is the density; T is the temperature; and R is the gas constant.

The magnitude of modified filler/polymer interactions has been expressed by a Flory–Huggins parameter (χ'_{23}). χ'_{23} has been successfully used in the characterization of series of polymer blends.[7,9,15,16] A large positive value indicates the absence of interactions or negligible interactions between components, a low value indicates favorable interactions, whereas a negative value indicates strong interactions.[17]

When a filled polymer is used as a stationary phase in a chromatographic column, subscripts 2 and 3 represent the polymer and filler, respectively. The interactions between modified silica and a polymer are expressed in terms of χ'_{23} as an indicator of the miscibility of the polymer blend. Therefore, χ'_{23} can be derived from the following:[18,19]

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

where φ_2 and φ_3 are the volume fractions of the polymer and filler in the blend and the second subscript of V_g identifies the nature of the column.

To obtain χ'_{23} for a polymer blend or composition with IGC, χ_{12}^{∞} values for all components have to be known. Therefore, three columns are usually prepared: two for single components and the third for a composition of the two components used. Another 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, and inlet pressure of the carrier gas and with the same test solutes.[9]

Values of χ'_{23}, determined by means of IGC, depend on the chemical structure of the solute, and it is a common phenomenon, although not allowed by theory.[14] It has been interpreted as a result of preferential interactions of the test solute with one of two components. This phenomenon for polymer blends was described by Fernandez-Sanchez et al.[14]

Zhao and Choi[17,20] also discussed the solvent-dependence problem of χ'_{23}. They discovered that the problem essentially originates from the improper choice of reference volumes used in the calculations of the binary interaction parameter between various solvents and the pure polymers as well as their blends. Traditionally, in the Flory–Huggins theory, the molar volume of the solvent (V_1) is usually taken as the reference volume (V_o). The problem occurs for ternary systems: differences in the values of the χ

TABLE II
Values of χ_{12}^{∞} for the 20% N2–PU System at Different Temperatures

Test solute	363 K	373 K	383 K	393 K	403 K
C_5	0.503	0.593	0.550	0.636	0.155
C_6	0.808	0.916	0.854	0.924	0.617
C_7	0.743	0.852	0.840	0.859	0.592
C_8	0.705	0.835	0.816	0.786	0.657
C_9	0.724	0.881	0.833	0.830	0.664
CH_2Cl_2	−0.099	0.066	0.086	0.211	−0.035
$CHCl_3$	−0.452	−0.233	−0.194	−0.153	−0.331
CCl_4	0.219	0.345	0.349	0.341	0.177
$C_2H_2Cl_2$	0.103	0.282	0.270	0.260	0.194

TABLE III
Values of χ_{12}^{∞} for the 20% N–PU Systems at Different Temperatures Calculated by the Zhao–Choi Procedure

	20% N1–PU					20% N2–PU				
Test solute	363 K	373 K	383 K	393 K	403 K	363 K	373 K	383 K	393 K	403 K
C_5	2.080	2.100	1.969	2.041	1.918	1.977	2.042	1.973	2.025	1.655
C_6	2.135	2.158	2.047	2.100	2.011	2.015	2.096	2.016	2.057	1.762
C_7	1.810	1.860	1.760	1.784	1.698	1.723	1.801	1.775	1.774	1.543
C_8	1.640	1.670	1.598	1.602	1.546	1.508	1.598	1.571	1.536	1.429
C_9	1.485	1.534	1.473	1.471	1.422	1.373	1.475	1.432	1.419	1.297
CH_2Cl_2	1.347	1.565	1.558	1.599	1.648	1.016	1.344	1.392	1.627	1.195
$CHCl_3$	0.359	0.563	0.585	0.699	0.783	0.064	0.424	0.502	0.580	0.336
CCl_4	1.035	1.122	1.069	1.104	1.118	0.829	1.000	1.006	1.002	0.803
$C_2H_2Cl_2$	1.510	1.645	1.577	1.610	1.668	1.218	1.506	1.488	1.473	1.373

parameter originate from the lattice size used. Zhao and Choi propose to use a common reference volume, which solves the problem.

In the Flory–Huggins theory, the Flory–Huggins parameter for blends (χ_{1m}) can be calculated with the following equations:

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

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

Plotting χ_{1m} versus $\varphi_2 \cdot \chi_{12} + \varphi_3 \cdot \chi_{13}$ [eq. (5)] gives a straight line with a slope of 1 and an intercept of $-\varphi_2 \cdot \varphi_3 \cdot ZC\chi'_{23}$, where $ZC\chi'_{23}$ denotes χ'_{23} determined with the Zhao–Choi procedure.

We propose to express the magnitude of modified filler/polymer interactions by the use of χ'_{23} and $ZC\chi'_{23}$.

EXPERIMENTAL

Materials

IGC experiments were used to examine the interactions of polymer–filler systems containing oligomeric poly(ether urethane) (PU), which was prepared by Dr. J. Jęczalik (average molar mass ~ 4200 g/mol). PU, having a two-end hydroxyl group and two urethane groups inside, was prepared with 2 mol of a triblock oxyetylene-oxypropylene-oxyetylene (EO–PO–EO) copolymer with a molecular mass of approximately 2000 containing approximately 95% PO units and with 1 mol of toluene diisocyanate (80/20 mixture of 2,4- and 2,6-isomers) with an average molar mass of approximately 174 g/mol. The polymer was filled with 5, 10, or 20 wt % carbonate–silicate fillers[21,22] modified with (1) *N*-2-aminoethyl-3-aminopropyltrimethoxysilane (N1; trade name U15D, UNISIL, Poland) and stearic acid (PPH Standard, Poland) (the N1-modified filler was characterized by a specific surface area of 160 m^2/g and a mean diameter of agglomerates of ca. 616 nm) or (2) octyl-

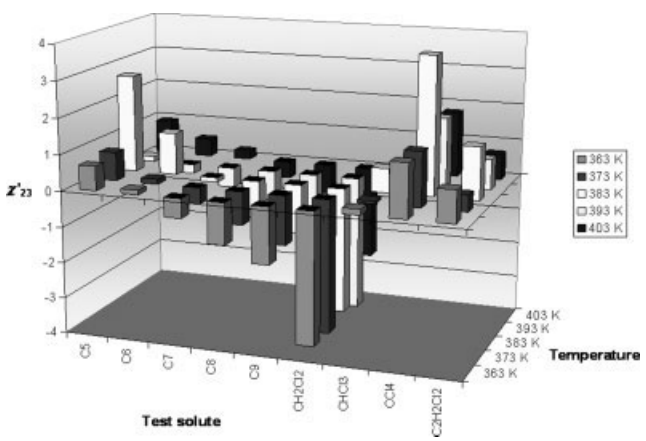


Figure 1 Values of χ'_{23} for 5% N1–PU.

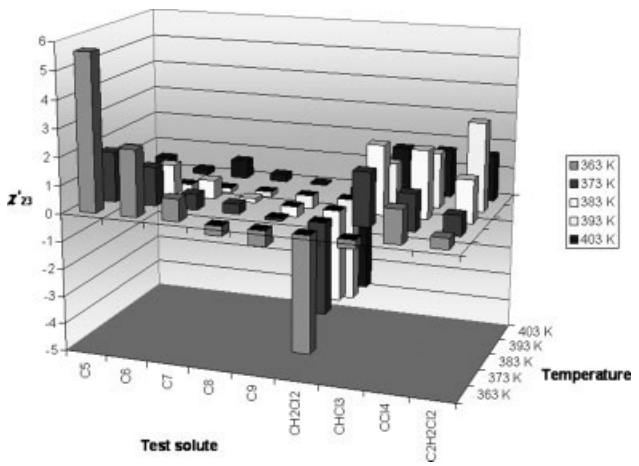


Figure 2 Values of χ'_{23} for 5% N2–PU.

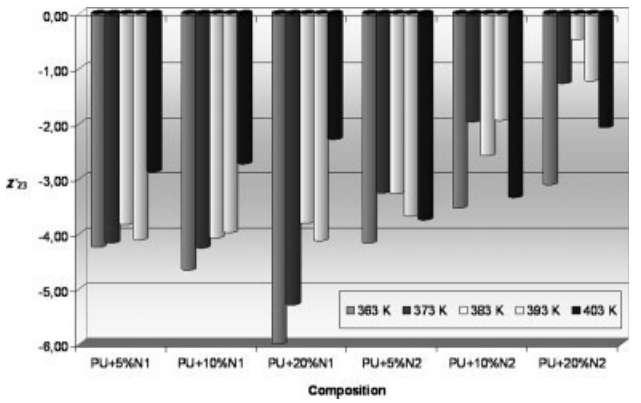


Figure 3 Comparison of the values of χ'_{23} for all of the compositions (with CH_2Cl_2 as the test solute).

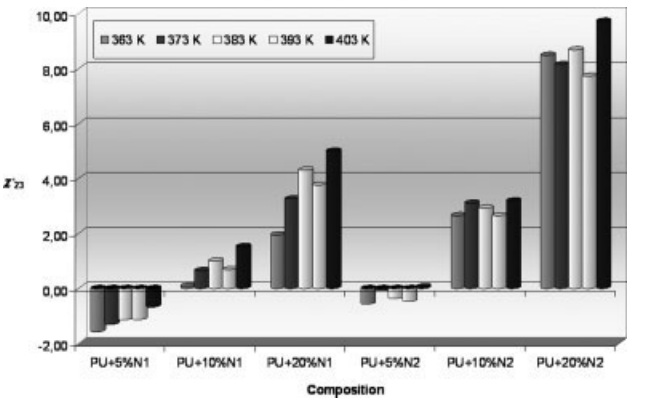
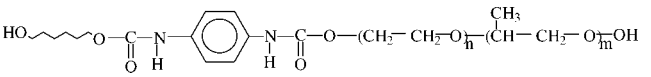


Figure 4 Comparison of the values of χ'_{23} for all of the compositions (with C_9 as the test solute).

silane (N2; trade name U222, UNISIL, Poland) and stearic acid (the N2-modified filler was characterized by a specific surface area of 160 m^2/g and a mean diameter of agglomerates of ca. 691 nm).

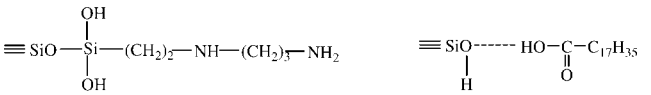
The abbreviation PU–20% N1 denotes PU filled with 20 wt % carbonate–silicate fillers modified with N1 and stearic acid.

The polymer has the following formula:



The following groups are present in the surface layers of the fillers:

- **N1**



- **N2**

All modifications (dry technique) and preparation of fillers were done by J. Grodzka. The amounts of the modifier in the fillers were 2 or 5 weight parts per 100 weight parts of filler. The carbonate–silicate filler, precipitated from a solution of sodium metasilicate and calcium hydroxide in the presence of gaseous CO_2, was placed in a mixer, and an appropriate amount of the modifier was added. The mixing was carried out for 1 h. The silanes were added at 2 weight parts per 100 weight parts of the filler (N1) or 5 weight parts per 100 weight parts of the filler (N2), and stearic acid was added at 2 or 5 weight parts per 100 weight parts of the filler. The modified particles were submitted to solvent extraction (Soxhlet) to remove unbounded coupling agents.

Conditions

Measurements were carried out with a Chrom5 (Kovo, Czech Republic) gas chromatograph equipped with flame ionization detector. Glass columns (100 cm × 0.4 mm i.d.) were packed with the support coated with the polymer or filled polymer. The polymer and compositions were coated from solution onto Chromosorb P AW DMCS at a 15 wt % loading. We also tested columns packed only with the modified filler. Columns were conditioned under helium at the maximum analysis temperature overnight before use. The following compounds were used as test solutes: pentane (C_5), hexane (C_6), heptane (C_7), octane (C_8), nonane (C_9), methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), and 1,2-dichloroethane ($C_2H_2Cl_2$). Small

TABLE IV
Values of the $ZC\chi'_{23}$ Parameter for the PU–N1 Systems

	PU + 5% N1			PU + 10% N1			PU + 20% N1		
Temperature (K)	Intercept	R^2	$ZC\chi'_{23}$	Intercept	R^2	$ZC\chi'_{23}$	Intercept	R^2	$ZC\chi'_{23}$
363	0.0009	0.9940	−0.0191	0.0015	0.9920	−0.0167	0.0025	0.9860	−0.0155
373	0.0014	0.9930	−0.0289	0.0016	0.9880	−0.0174	0.0021	0.9870	−0.0129
383	0.0020	0.9960	−0.0413	0.0026	0.9890	−0.0290	0.0023	0.9920	−0.0145
393	0.0016	0.9930	−0.0342	0.0020	0.9910	−0.0224	0.0018	0.9920	−0.0113
403	0.0006	0.9950	−0.0125	0.0012	0.9910	−0.0129	0.0013	0.9900	−0.0084

TABLE V
Values of the $ZC\chi'_{23}$ Parameter for PU–N2

	PU + 5% N2			PU + 10% N2			PU + 20% N2		
Temperature (K)	Intercept	R^2	$ZC\chi'_{23}$	Intercept	R^2	$ZC\chi'_{23}$	Intercept	R^2	$ZC\chi'_{23}$
363	0.0032	0.9890	−0.0664	0.0025	0.9900	−0.0277	0.0019	0.9940	−0.0119
373	0.0018	0.9840	−0.0373	0.0011	0.9860	−0.0127	0.0016	0.9860	−0.0099
383	0.0023	0.9880	−0.0486	0.0024	0.9830	−0.0266	0.0020	0.9930	−0.0123
393	0.0026	0.9860	−0.0543	0.0014	0.9930	−0.0155	0.0018	0.9910	−0.0111
403	0.0016	0.9950	−0.0336	0.0015	0.9940	−0.0168	0.0004	0.9970	−0.0025

volumes (0.5 μL) of vapor of the probes were injected manually to achieve the infinite dilution conditions. The injection of each test solute was repeated five times. The temperatures of the experiment were as follows: injector, 423 K; detector, 423 K; and column oven, 363, 373, 383, 393, and 403 K. The helium flow rate was 40 mL/min.

RESULTS

Values of χ_{12}^{∞} calculated from eq. (2) on the basis of the Flory–Huggins equation of state for compositions with 20% of both fillers are presented in Tables I and II. Positive values of χ_{12}^{∞} indicate weak interactions observed for almost all test solutes interacting with both compositions. Negative values were found only for $CHCl_3$, indicating strong specific interactions between this test solute and the examined material. This effect is somewhat unexpected as the strongest interactions should occur for compounds with the highest value of the dipole moment, that is, CH_2Cl_2 and/or $C_2H_2Cl_2$. The increase in the column temperature resulted in the weakening of the test solute/composition interactions (increase of the χ_{12}^{∞} values).

Values of χ_{1m}^{∞} found with the Zhao and Choi equation [eq. (4)] are different from those presented in Tables I and II, and they are collected in Table III. Values obtained from the standard equation [eq. (2)] are lower than those obtained with the Zhao–Choi equation [eq. (4)]. This may be caused by the high difference between the molar volumes of the components used in the calculations. The confidence interval of all calculated values is lower than ±0.05.

Values of χ'_{23} were calculated in the traditional way and compared with those from procedures proposed by Zhao and Choi. Values obtained from the basic (classic) equation [eq. (3)] for the examined compositions (5% N–PU) are given in Figures 1 and 2. Values of χ'_{23} are solute-sensitive. Negative values of χ'_{23} were obtained for some of the test solutes, indicating strong interactions between the polymer and filler. However, positive χ'_{23} values found, for example, with the use of $CHCl_3$ or CCl_4 suggest weak or no interactions. This might be a source of misunderstanding.

Therefore, we have to determine which of the test solutes is representative: nonpolar alkane, dichloromethane, or another test compound. It would be arbitrary and might lead to erroneous conclusions. Values of χ'_{23} for all investigated compositions, calculated with the use of nonpolar (C_9) and polar (CH_2Cl_2) test solutes, are presented in Figures 3 and 4, respectively. As shown in Figure 3, the values for all compositions are negative, but when we used C_9, only two of the compositions gave negative values of χ'_{23}. Thus, the conclusions really depend on the test solute used in the experiment.

To eliminate the solvent dependence of χ'_{23} values (from the basic equation), we recalculated experimental data according to the Zhao–Choi procedure [eq. (5)]. Values of $ZC\chi'_{23}$ are presented in Tables IV and V. In all cases, we obtained only one value for each composition. All $ZC\chi'_{23}$ values are negative. All these values suggest the presence of a strong interaction between the modified filler and polymeric matrix. This observation is consistent with that from an analysis of χ'_{23} data for most of the test solutes in the classic procedure.

Values of $ZC\chi'_{23}$ depend on the temperature (Figs. 5 and 6). In almost all cases, the values increase with

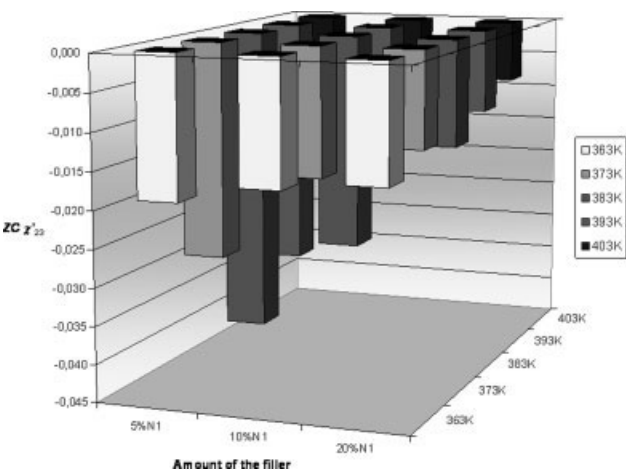


Figure 5 Influence of the amount of filler N1 on the $ZC\chi'_{23}$ values.

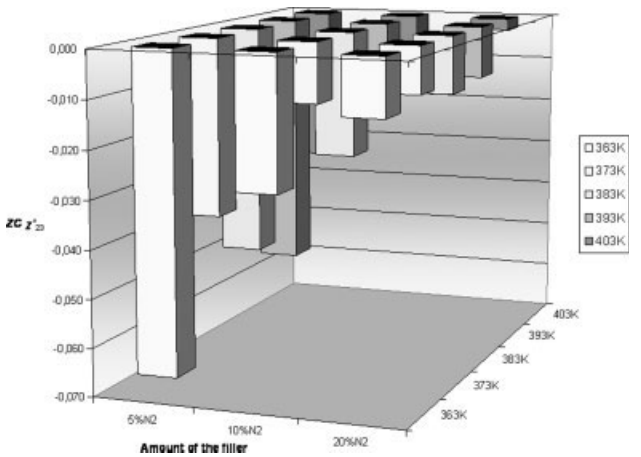


Figure 6 Influence of the amount of filler N2 on the $ZC\chi'_{23}$ values.

an increase in the temperature. This means that the magnitude of the interactions decreases with increasing temperature. The addition of the filler to the composition results in higher $ZC\chi'_{23}$ values, that is, weaker filler–polymer interactions.

For the N1–PU compositions, the addition of the filler causes an increase in $ZC\chi'_{23}$ values. This means that the strongest interactions between the polymer and N1 filler are observed for a 5% addition. The same influence of the filler content was observed for the N2–PU composition. Here the influence of the addition of the filler is also clearly visible. The strongest filler–polymer interactions (the lowest $ZC\chi'_{23}$ value) were found for the 5% N2–PU composition at 363 K (Fig. 6).

CONCLUSIONS

χ'_{23} values depend on the chemical nature of the test solute. The lowest values of χ'_{23} were obtained for dichloromethane. The application of the procedure proposed by Zhao and Choi allowed us to minimize the $\Delta\chi'_{23}$ effect; that is, the χ'_{23} values did not depend on the nature of the test solute. With χ'_{23} values, it was possible to investigate the changes in the magnitude of interactions between the components of the composition resulting from changes in the filler properties, its amount, and the temperature. An increase in the temperature caused an increase in the χ'_{23} values, and this indicated a decrease in the filler–polymer interactions: the lowest values were obtained at 363 K. The addition of a filler caused an increase in χ'_{23} values, and this indicated the weakening of interactions (the lowest values were obtained for 5% addition of both fillers). Stronger interactions between the components were observed for the composition with the N2 filler (lower values).

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