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DOI: dx.doi.org/10.14314/polimery.2013.869

# Characterization of composites interactions by chromatographic and non-chromatographic methods

**Summary** — The scale of the interactions in polymer systems (blend or composition) is an important factor used in the prediction of the stability of the material. The article presents some of the techniques used to determine the compatibility of the material. The author described techniques of P-V-T (pressure-volume-temperature), SAXS (small angle X-ray scattering), SANS (small angle neutron scattering), TIPS (thermal induced phase separation) and IGC (inverse gas chromatography) to determine the parameters of miscibility. The IGC technique plays an increasing role in the characterization of polymer systems.

**Keywords**: Flory-Huggins parameters, IGC, interactions in blends/compositions.

## CHARAKTERYSTYKA KOMPOZYCJI POLIMEROWYCH ZA POMOCĄ TECHNIK CHROMATOGRAFICZNYCH I NIECHROMATOGRAFICZNYCH

**Streszczenie** — Siła oddziaływań w układach polimerowych (mieszaninach lub kompozycjach) jest ważnym czynnikiem wyznaczającym stabilność materiału. W artykule przedstawiono wybrane techniki używane do określania kompatybilności materiału. Omówiono wykorzystanie technik: P-V-T (zależność ciśnienie-objętość-temperatura), SAXS (małokątowe rozpraszanie promieniowania X), SANS (małokątowe rozpraszanie neutronów), TIPS (termicznie indukowana separacja faz) oraz IGC (inwersyjna chromatografia gazowa) odgrywającą coraz większą rolę w charakteryzowaniu układów polimerowych do wyznaczania parametrów mieszalności.

**Słowa kluczowe**: parametry Flory-Hugginsa, IGC, oddziaływania w mieszaninach/kompozycjach.

## INTRODUCTION

Nowadays, composite materials play an increasingly important role in many industries. These materials usually comprise a polymer matrix in which small filler particles are thoroughly dispersed. Addition of filler lowers the cost and also improve the tensile strength of the base resin. Obviously, the filler must be well dispersed in the matrix to avoid zones of weaker cohesion. Usually, those fillers are chemically treated to enhance the filler and polymer interaction [1]. Although the filler content, chemical character of the components and filler characteristics significantly influence the rheological and mechanical properties of polymer composites, any change in polymer/filler interaction also has a considerable effect on these properties [2, 3].

With the growing interest in polymer composition a variety of experiments are used to determine material compatibility. Only a few techniques can give quantitative information about the change in free energy when mixing two components. It has been shown that data from P-V-T experiments might be successfully used in the prediction of the miscibility of polyolefin blends [4]. Interaction parameter for the components of polymer blends was also determined with small angle X-ray scattering (SAXS) [5—7], thermal induced phase separation (TIPS) [8] and small angle neutron scattering (SANS) [9—13]. It is worth to note the increasing role of inverse gas chromatography (IGC) [14]. During the years this method has become an accurate, reliable and fast method for physicochemical characterization of polymer systems.

## INVERSE GAS CHROMATOGRAPHY

The term inverse indicates that the examined material (polymer, composition, blend, *etc.*) is placed in a chromatographic column and studied using volatile test solutes [15]. To obtain information about miscibility of solutes (of different chemical natures) on examined materials retention parameters are measured [16].

The usefulness of IGC for determining polymer — small molecule interactions is well established [14, 16—18]. Measured retention parameters (*e.g.* $V_g$ — specific retention volume) are easily recalculated to Flory-Huggins parameters, according to the equation [15, 16]:

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

where: *1 denotes the solute and 2 or 3 denotes examined materials,* $M_1$ *— the molecular weight of the solute,* $p_1^o$ *— the saturated vapor pressure of the solute,* $B_{11}$ *— the second virial coefficient of the solute,* $V_i$ *— the molar volume,* $\rho_i$ *— the density, R — the gas constant.*

For the case of the mixture (polymer-filler composition) equation (1) could be rearranged into [19, 20]:

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

where: $\varphi_2$ *and* $\varphi_3$ *— the volume fractions of polymer and filler, and index m means a composition.*

The Flory-Huggins interaction parameter $\chi_{12}^{\infty}$ is a measure of the free energy in the interaction between the probe and the examined material.

Inverse gas chromatography was used to characterize the interaction between components of composition (polymer-polymer, polymer-filler, filler-filler). The interaction between the two components of composition is expressed in terms of $\chi'_{23}$ calculated from [19, 20]:

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

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

To obtain $\chi'_{23}$ for a polymer blend or composition utilizing IGC, values of $\chi_{12}^{\infty}$ for all components have to be known [16, 19].

The Flory-Huggins $\chi'_{23}$ parameter was used in the characterization of the series of polymer blends [14, 16, 21, 22]. A large positive value indicates unfavorable interaction, a low value indicates favorable interaction, while a negative value indicates a rather strong specific interaction [23].

Values of the Flory-Huggins $\chi'_{23}$ parameter depend on the chemical structure of the solute and it is a common phenomenon, although not allowed by the theory [24]. It has been interpreted as arising for preferential interaction with one of two types of components. This phenomenon for polymer blends was described by Fernandez-Sanchez *et al.* [24].

Deshpande and Farooque [25] were the first to observe the probe dependence of polymer-polymer interaction and tried to develop a method to evaluate a probe-independent interaction.

Zhao and Choi [26, 27] also paid much attention to the solvent dependence problem. Authors proposed to use two equations:

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

and

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

Equation (5) describes a plot of $\chi_{1m}$ versus ($\varphi_2 \cdot \chi_{12} + \varphi_3 \cdot \chi_{13}$) representing a straight line with a slope 1 and an intercept of – $\varphi_2 \cdot \varphi_3 \cdot \chi'_{23}$.

Benabdelghani *et al.* [28, 29] investigated the miscibility behavior of blends by IGC. They determined the polymer-polymer interaction parameter $\chi'_{23}$ and they also observed a large influence of the test solute used in IGC experiments on the determined values. This influence has been described as $\Delta\chi$ effect, related to non-random partitioning of the probe. Authors applied two simple methods to obtain the true polymer–polymer interaction parameter in the PSMA-12/PPO system [poly(styrene-*co*-maleic anhydride)/poly(phenylene oxide)]. They used a method proposed by Deshpande and Farooque [30].

By plotting the left-hand side of Eq. (6) *vs.* $\varphi_2 \cdot (\chi_{12}^{\infty} - \chi_{13}^{\infty}) / V_1$ the interaction parameter can be obtained from the intercept.

$$\frac{\chi_{1(23)}^{\infty} - \chi_{13}^{\infty}}{V_1} = \varphi_2 \cdot \frac{\chi_{12}^{\infty} - \chi_{13}^{\infty}}{V_1} - \varphi_2 \cdot \varphi_3 \frac{\chi'_{13}}{V_2} \tag{6}$$

The second procedure based on Huang's [31, 32] proposal — the rearrangement of Eq. (6) into the following form:

$$\frac{\chi_{1(23)}^{\infty}}{V_1} = \frac{\varphi_2 \cdot \chi_{12}^{\infty} + \varphi_3 \cdot \chi_{13}^{\infty}}{V_1} - \varphi_2 \cdot \varphi_3 \frac{\chi'_{23}}{V_2} \tag{7}$$

A linear plot of the left-hand side *vs.* $\varphi_2 \cdot \chi_{12}^{\infty} + \varphi_3 \cdot \chi_{13}^{\infty} / V_1$ allows the determination of polymer-polymer interaction parameter from the intercept at $\varphi_2 \cdot \chi_{12}^{\infty} + \varphi_3 \cdot \chi_{13}^{\infty} / V_1 = 0$. Benabdelghani *et al.* [28] transformed equation (7) to form (8) using only experimental measured magnitudes, avoiding the error introduced by others ($V_1$, $p_1^o$ and $B_{11}$) while calculating $\chi_{1i}$:

$$\frac{1}{V_1} \ln\left(\frac{V_{gm}}{v_m}\right) = \frac{1}{V_1} \cdot \left[\varphi_2 \ln\left(\frac{V_{g2}}{v_2}\right) + \varphi_3 \ln\left(\frac{V_{g3}}{v_3}\right)\right] + \varphi_2 \varphi_3 \frac{\chi'_{23}}{V_2} \tag{8}$$

where: $v_m = v_2 \cdot w_2 + v_3 \cdot w_3$, $v_i$ *— specific volume and,* $w_i$ *— the weight fraction of polymer in blend.*

## P-V-T EXPERIMENTS

The relationship between pressure, volume and temperature (P-V-T) for polymeric materials is a subject of importance to polymer scientists and engineers, particularly from a process design standpoint. Pressure-volume-temperature (P-V-T) information for a variety of pure polymers at temperatures above the melting point $T_m$ of crystalline polymers or the glass transition temperature $T_g$ for amorphous polymers has been established through both empirical and theoretical studies [33, 34].

Numerous theoretical equations of state for polymer liquids have been developed [35—41] over the past couple of decades. Equation of state (EOS) is a mathematical relation between volume, pressure, temperature and composition [42].

The Flory-Orwoll-Vrij (FOV) [34] and the Sanchez-Lacombe (SL) [40, 41] lattice-fluid equations of states are both significantly less accurate over the wider pressure range. FOV equation of state can be expressed in reduced form as:

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{\frac{1}{3}}}{\left(\tilde{V}^{\frac{1}{3}}-1\right)} - \frac{1}{\tilde{V}\tilde{T}} \tag{9}$$

where: $\tilde{P}$, $\tilde{T}$ *and* $\tilde{V}$ *— reduced parameters, calculated as follows*:

$$\tilde{T} = \frac{T}{T^*};\ \tilde{P} = \frac{P}{P^*};\ \tilde{V} = \frac{V}{V^*} \tag{10}$$

SL EOS is derived based on lattice fluid theory which allows for vacancies in the lattice and assumes the polymer has a flexible liquid structure. The reduced form of SL EOS is through equation:

$$\tilde{P} = -\tilde{\rho}^2 - \tilde{T}\left[\ln(1-\tilde{\rho}) + \left(1-\frac{1}{r}\right)\tilde{\rho}\right] \tag{11}$$

In the above relations, $\tilde{P}$, $\tilde{\rho}$, $\tilde{T}$ and $\tilde{V}$ are reduced parameters. They are calculated from the characteristic reducing parameters $P^*$, $T^*$, $V^*$ and $\rho^*$ as follows:

$$1/\tilde{\rho} = \frac{V}{V^*};\ \tilde{T} = \frac{T}{T^*};\ \tilde{P} = \frac{P}{P^*};\ \tilde{V} = \frac{V}{V^*};\ r = \frac{MP^*}{RT^*\rho^*} \tag{12}$$

where: $r$ *— the fraction of occupied lattice sites by a molecule composed of* $r$ *segments or „mers" and* $M$ *is the molecular weight*.

To understand the interaction between molecules, which play a major part in determining properties of materials, we need to estimate the forces between molecules. A way to determine the intermolecular forces of small molecules involves measuring their cohesive energy density (*CED*) [4, 28, 30, 43, 44]. There are many methods and techniques available to determine the solubility. The most popular methods used to determine solubility is the gravimetric method using the magnetic suspension balance (MSB) system and theoretical EOS calculations.

The solubility parameter is the square root of the *CED*. The solubility parameter formalism also provides a very useful approach for predicting the mutual miscibility of two polymers by measurement of isobaric thermal expansion coefficients and isothermal compressibility. The internal pressure, which is a derivative form of cohesive energy with respect to *V*, measures the instantaneous intermolecular interaction energy associated with an isothermal expansion of the liquid. Thus,

$$CED = \left(\frac{\Delta U_{vap}}{V}\right) = \delta^2 \tag{13}$$

$$CED \cong \pi = \left(\frac{\partial U}{\partial V}\right)_T \tag{14}$$

$(\partial U/\partial V)_T$ can be related to other thermodynamic identities such as:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P = T\left(\frac{\alpha}{\beta}\right) - P \tag{15}$$

where: $\alpha = (1/\underline{V})(\delta\underline{V}/\delta T)_P$ *— isobaric thermal expansion coefficient,* $\beta = -(1/\underline{V})(\delta\underline{V}/\delta P)_T$ *— isothermal compressibility,* $P$ *— atmospheric pressure,* $\underline{V}$ *— specific volume*.

The internal pressure is generally much greater than the ambient pressure so:

$$\delta \cong \left\{T\left(\frac{\alpha}{\beta}\right)\right\}^{\frac{1}{2}} \tag{16}$$

The quantities of α and β can be obtained experimentally from the slopes of isotherm and isobars in PVT experiment. The cohesive energy density and internal pressure represent the intermolecular forces of a pure component. By closely matching the cohesive energy densities of two polymers, miscible polymer pairs can be identified, especially in nonpolar hydrocarbon polymers [4]:

$$X_{12} = (\delta_1 - \delta_2)^2 \tag{17}$$

where: $\delta_1$, *the solubility parameter at certain temperature, may be obtained from the experimental PVT data*.

The entropy of mixing for a high molecular weight polymer pair is quite small so that $\chi_{12}$ (interaction energy density) usually determines the sign of free energy of mixing. A polymer pair will be miscible when the solubility parameter difference between polymers from this pair is less than 0.3 $MPa^{1/2}$.

## SMALL ANGLE X-RAY SCATTERING

Small angle X-ray or neutron scattering (SAXS or SANS) are experimental techniques used to derive size and shape parameters of large molecules which cannot be determined by other methods (such as microscopy or X-ray diffraction) or for studying the morphology of complex aggregates and polymeric systems as a function of process parameters [45, 46].

Both X-ray and Neutron Scattering is based on the same physical phenomenon, *i.e.*, scattering due to differences in scattering mass density for X-rays and neutrons, respectively, between the solute and the solvent or indeed between different molecular constituents.

Synchrotron small angle X-ray scattering can be used to measure the Flory-Huggins interaction parameter. The binary interaction parameter (χ) can be obtained *via* the de Gennes random phase approximation (RPA). The RPA provides an expression for the total structure factor, $S(q)$, of a homogeneous blend as it was proposed [47, 48]:

$$\frac{1}{S(q)} = \frac{1}{V_1 \cdot N_1 \cdot \phi_1 \cdot S_D\,(qR_{g1})} + \frac{1}{V_2 \cdot N_2 \cdot \phi_2 \cdot S_D\,(qR_{g2})} - \frac{2 \cdot \chi}{V_o} \tag{18}$$

where: $\phi_i$, $R_{gi}$, $N_{n,i}$ — *the volume fraction, radius of gyration and number-average degree of polymerization of the component i;* $V_i$ — *the monomer molar volume;* $V_o$ — *a reference volume* $S_D(x)$ *which denotes the weight-averaged Debye function for polydisperse chains*.

This technique was used to studies of nanosilica/polyurethane composites [49], for characterization of biodegradable poly(L-lactide)/poly(ε-caprolactone)-montmorillonite nanocomposites [50].

## SMALL ANGLE NEUTRON SCATTERING

Small angle neutron scattering (SANS) is one of the methods used to obtain the Flory-Huggins interaction parameter for polymer blends because of high contrast between labeled and unlabeled spices. $\chi$ parameter can be determined by fitting the scattering intensity profiles of single-phase blends to the well-established random-phase approximation. The scattering interaction parameter $\chi_S$ is different from the interaction parameter ($\chi_F$) in the Flory-Huggins theory. That parameter can be written as the derivative form of the Flory-Huggins interaction parameter [51]:

$$2\chi_S = 2\chi_F - 2 \cdot (1 - 2\phi) \cdot \frac{\partial \chi_F}{\partial \phi} - \phi \cdot (1 - \phi) \cdot \frac{\partial^2 \chi_F}{\partial \phi^2} \tag{19}$$

where: $\chi_S$ — *the scattering interaction parameter, which is a function of composition and temperature and can be obtained by modeling the experimental results of SANS [52],* $\phi$ — *the volume fraction*.

Both parameters $\chi_F$ and $\chi_S$ are dependent on the reference volume. SANS was used to probe the thermodynamic interactions in multicomponent polymer blends including ternary blends containing two homopolymers and a block copolymer, and a blend of two block copolymers. Lin *et al.* [53] used this technique for the study of model polyolefins-poly(ethylbutylene) and poly(ethylbutylene) block poly(methyl-butylene) copolymer. Obtained $\chi$ parameters were independent of blend composition, molecular weight and molecular architecture of the components.

Balsara *et al.* [54, 55] determined the Flory-Huggins interaction parameter from data obtained from SANS experiments for binary blends of polyisobutylene and deutered polybutadiene. Small-angle neutron scattering (SANS) was also used to study the changes of segmental interactions and chain conformation due to the formation of lithium-PMMA complexes in polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) copolymers as a function of temperature and the percentage of carbonyl groups coordinated with lithium ions [56].

## DIFFERENTIAL SCANNING CALORIMETRY

In last two decades, the Flory-Huggins interaction parameter was determined using the melting point depression method for crystal-containing polymers by differential scanning calorimetry (DSC) [57, 58]. A single glass transition temperature observed for the blends indicates the miscibility of the components. Measurement of the melting temperature $T_m$ depression for the blends allowed determination of the Flory-Huggins interaction parameter ($\chi_{12}^{\infty}$) for the two polymers in the melt using the Nishi-Wang equation [59—61]:

$$\frac{1}{T_m} - \frac{1}{T_m^o} = -\left(\frac{RV_2^u}{V_1^u \Delta H_2^u}\right)\chi_{12}(1 - V_2)^2 \tag{20}$$

where: *the subscript 1 identified with the amorphous polymer and 2 with the crystalline polymer,* $T_m^o$ — *the equilibrium melting point,* $V$ — *the volume fraction,* $V^u$ — *the molar volume of the repeating units,* $\Delta H_2^u$ — *the enthalpy of fusion per mole of repeating unit*.

Equation (20) describes the melting point depression due to mixing of a crystalline polymer and an amorphous polymer [59].

The Flory-Huggins model applied to a tertiary system in equilibrium can be expressed as follows [62]:

$$\frac{1}{T_m} - \frac{1}{T_m^o} = \left(\frac{R}{\Delta H_u}\frac{V_u}{V_1}\right)\left[\phi_1 + \left(\frac{\phi_3}{x_3}\right) + \chi_{13}\phi_1\phi_3 - \left[\chi_{12}\phi_1 + \chi_{23}\left(\frac{\phi_3}{x_3}\right)\right](\phi_1 + \phi_3)\right] \tag{21}$$

where: $\Delta H_u$ — *the heat of fusion of a polymer repeating unit,* $T$ — *the absolute temperature,* $R$ — *the gas constant,* $V_1$ *and* $V_u$ — *the molar volumes of the diluents and the repeating unit of the polymer;* $\phi_1$, $\phi_2$, *and* $\phi_3$ — *the volume fractions;* $x_3$ — *the number of segments per molecule of solute, and* $\chi_{12}$, $\chi_{13}$, *and* $\chi_{23}$ — *the (enthalpic) interaction parameters*.

The polymer-polymer interaction parameters obtained from thermodynamic melting temperature depression analysis should be negative, exhibiting dependence on the blend composition [63].

## CONCLUSIONS

The study of properties of multicomponent polymer systems, such as polymer-polymer blends and domain structured block copolymers, is currently attracting wide research interest.

Miscible blends are of particular interest because they may exhibit a continuously variable spectrum of properties and price, across the composition range of the single phase behavior. Determining whether a particular pair of polymers is miscible is possible by many techniques (Table 1). The criterion of miscibility used most frequently is the occurrence of a single, well-defined glass transition for the mixture. This method is, however, of limited utility for systems in which pure species possess similar glass transition temperatures. Microscopic examination

**Table 1. Examples of studies on polymer blends with described techniques**

| No. | Polymer blend | Type of experiment | Comment | Ref. |
|---|---|---|---|---|
| 1. | PVC/MMVP | IGC and DSC | IGC as a method for describing the miscibility of the blend, where components have similar $T_g$ values | [64] |
| 2. | Polyolefins | P-V-T | the solubility parameter maps | [4] |
| 3. | Symmetric star polystyrenes | P-V-T | bulk thermodynamic properties — used to calculate the cohesive energy density (*CED*) | [65] |
| 4. | Highly concentrated native wheat starch mixtures | DSC, WAXS | quantitative description of the degree of starch gelatinization/melting as a function of the starch-water-solute ratio and temperature | [62] |
| 5. | PVC/PMMA blends | DSC and FT-IR | — miscibility is due to a specific interaction of hydrogen bonding type between carbonyl groups (C=O) of PMMA and hydrogen from (CHCl) groups of PVC;<br>— determination of the $T_g$ — for miscible polymers, a single $T_g$ is observed | [66] |
| 6. | Composite of polyethylene/ poly(vinyl acetate) | WAXS, SAXS, DSC, ATR-FT-IR | — results indicate that PVAc is generated in the amorphous regions of PE substrate;<br>— measurement showed that PE and PVAc were blended at the nanometer level | [67] |
| 7. | Binary blends of polyisobutylene and deuterated polybutadiene | SANS | the Flory-Huggins interaction parameter, $\chi$, was determined by fitting the scattering intensity profiles of single-phase blends to the well-established random-phase approximation | [54] |
| 8. | Poly(2,2,3,3,3-pentafluoropropyl methacrylate) (PPFPMA) | IGC (DSC TGA FT-IR) | — IGC as a tool for the thermodynamic characterization of PPFPMA;<br>— the glass transition temperature of PPFPMA is 62 °C measured by DSC | [68] |

and particularly scattering experiments also can be used profitably to ascertain the number of phases present in a mixture.

Although numerous methods have been developed for such purposes, only a few of them can be used to obtain thermodynamic parameters relevant to the miscibility issue. Among the frequently used techniques, inverse gas chromatography (IGC) has gained popularity in recent years because of its simplicity, rapidity, and the general availability of GC equipment.

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*Received 26 XI 2012.*