Journal of Thermal Analysis, Vol. 41 (1994) 1237-1243

EVALUATION OF THE FLORY-HUGGINS INTERACTION PARAMETER FOR POLY(STYRENE-co-ACRYLO-NITRILE) AND POLY(METHYL-METH-ACRYLATE) BLEND FROM ENTHALPY OF MIXING MEASUREMENTS

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Abstract

A direct determination of enthalpy of mixing (ΔH_{mix}) is of interest in predicting miscibility in polymer – polymer systems. Such measurements present, however, working difficulties, so a reliable indirect approach has been attempted. The enthalpy of mixing ΔH_m is obtained by application of Hess law to heat of solution measurement for blends and their components in a common solvent.

For SAN/PMMA blend, corresponding to the weight ratio 50:50, the experiments were performed by the Hess law approach at 29.4 and 49.3°C on dilute polymer solutions, for various concentrations, getting very good correlation data. This leads to a negative value of the interaction parameter $FH\chi_{(1,2)}$ and by ΔG_{mix} diagram it is possible to make a comparison for each temperature in accordance with the LCST behaviour of these mixtures.

Keywords: *FHχ* interaction parameter, polymer blends, calorimetry, enthalpy of solution, Hess cycle, styrene copolymers blends, PMMA blends

Introduction

Theoretical overview

To make possible an exhaustive interpretation of the properties of polymer mixtures such as polymer blends, it is necessary that phase boundaries and thermodynamic functions of state, related to the mixing process, are defined.

In order to achieve this purpose a first characterization, from the thermodynamic point of view, requires determination of the free energy of mixing ΔG_{mix} curve as a function of composition and temperature T.

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$$\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}} \qquad (1)$$

It is well known that for high molecular weight systems, such as polymer solutions, the entropic contribution ΔS_{mix} in the Eq. (1) is negligible with respect to low molecular weight systems [1, 2], so the enthalpic term ΔH_{mix} will therefore be dominant.

Several expressions for the calculation of ΔG_{mix} have been proposed in the recent years, but the simplest one is represented by the Flory-Huggins equation, which may read as a sum of a combinatorial and an interaction term [3, 4] and requires the knowledge of the interaction parameter $\chi_{(1,2)}$ as follows [5,6]:

$$\Delta G_{\mathrm{mix}}/RT = [(\varphi_1/N_1)\ln\varphi_1 + (\varphi_2/N_2)\ln\varphi_2 + \varphi_1\varphi_2\chi_{(1,2)}] \qquad (2)$$

where φ_1 and φ_2 are volume fraction of polymer 1 and 2 whose numbers of segments are N_1 and N_2 respectively.

The Eq. (2) gives reliable predictions of phase separation in case of positive values for $\chi_{(1,2)}$, that is when this latter term outweighs the favourable combinatorial contribution to the free energy of mixing [7].

In this work poly-methylmethacrylate (PMMA) and poly(styrene-co-acrylonitrile) (SAN) blend has been investigated by measuring the heat of solution of the blend and of its components in a suitable solvent and calculating ΔH_{mix} by the Hess Law approach [2, 8].

Hess Law is given by the following expression:

$$\Delta H_{\mathrm{mix}(1,2)} = \Delta H_1^s + \Delta H_2^s - \Delta H_{\mathrm{blend}}^s + \Delta H_{\mathrm{mix}}^s \qquad (3)$$

where ΔH_i^s is the heat of solution of the i component: $\Delta H_{\mathrm{blend}}^s$ is the heat of solution of a blend containing components 1 and 2 respectively and $\Delta H_{\mathrm{mix}}^s$, corresponding to the two solutions 1 and 2 together, can be considered of negligible amount for sufficiently dilute solutions.

The main disadvantage of the above mentioned method lays in the limited precision attainable in the measurements, because of the relatively small weight of $\Delta H_{\mathrm{mix}(1,2)}$ with respect to the terms on the right hand of the Eq. (3) and the relatively slow dissolution process of the polymers. In order to overcome this complication it is advisable, first, to operate at low concentration to minimise viscosity effect, secondly to employ a sensitive conduction calorimeter such as SETARAM C80/D to perform measurements whose reproducibility is <1% [9].

Experimental

Materials and samples

The polymer systems employed in this study are based on poly(styrene-co-acrylonitrile) (SAN), containing 24% w/w of acrylonitrile synthesized by suspension polymerization: its *Mw*, determined by GPC, is 115.000 and *Mw*/*Mn*= 1.92. For PMMA (VEDRIL 7) the *Mw* is 94.000 and *Mw*/*Mn* = 1.49. Blend corresponding to the weight ratio 50:50 were prepared by a Brabender mixer Plasti-Corder PL2000 at 220–230 °C and 50 rpm.

Technique

The calorimetric measurements of the heats of solution of the 50:50 PMMA/SAN blend and the pure polymers in chloroform have been performed by a SETARAM C80/D heat flux calorimeter [10, 11], requiring particular stainless steel cells, reversal mixing type, which enable them to keep the two components separated by a PTFE membrane, till the equilibrium state has been reached. In order to obtain complete mixing between the components, the above mentioned vessels are equipped with a rod, whose bottom is provided by sharp-edged impeller that permits the membrane to be torn and to make stirring. The volume of the cells is of 2.0 cm^3 and their pressure capacity of 20 bars. Measurements are attained both at 29.4 and 49.3°C for each concentration till a maximum of 6% w/w of polymer in solvent.

Results and discussion

The results are summarized in Table 1 where the values of the interaction parameters $\chi_{(1,2)}$ are reported together with the mixing enthalpies whose elaboration requires the expression for the Free Energy of mixing, based on the Flory-Huggins treatment [12].

As far as the experimental enthalpies of solution ΔH^s_{SAN} , ΔH^s_{PMMA}, ΔH^s_{BLEND} is concerned, in Table 1 the slopes of the linear correlations for 29.4 and 49.3°C are also specified, as showed in Figs 1–2.

The reference molar volume used in calculations is the average of molar volume of the polymer units, for each components, at the considered temperatures.

The standards deviation of calorimetric values, from the linear regressions, is <0.1%. This is important and represents the power of the method which requires very high precision and reproducibility of the experimental data, but, at the same time, gives a good demonstration of the linearity of ΔH_i^s with the concentration in the considered field.

Table 1 Calorimetric data for SAN/PMMA, chemical-physical properties of materials [13] and linear correlation slopes for enthalpy of mixing data in chloroform

T /°C	$\Delta H_{\mathrm{mix}(1,2)}$ / J·g^{-1}	$\chi_{(1,2)}$	ρ / g·cm^{-3} SAN	ρ / g·cm^{-3} PMMA	Slope $\Delta H^{s}_{\mathrm{SAN}}$	Slope $\Delta H^{s}_{\mathrm{PMMA}}$	Slope $\Delta H^{s}_{\mathrm{BLEND}}$
29.4	–1.94E–03	–2.9E–04	1.066	1.187	0.622	0.708	0.663
49.3	–2.00E–04	–2.7E–05	1.050	1.182	0.529	0.603	0.566

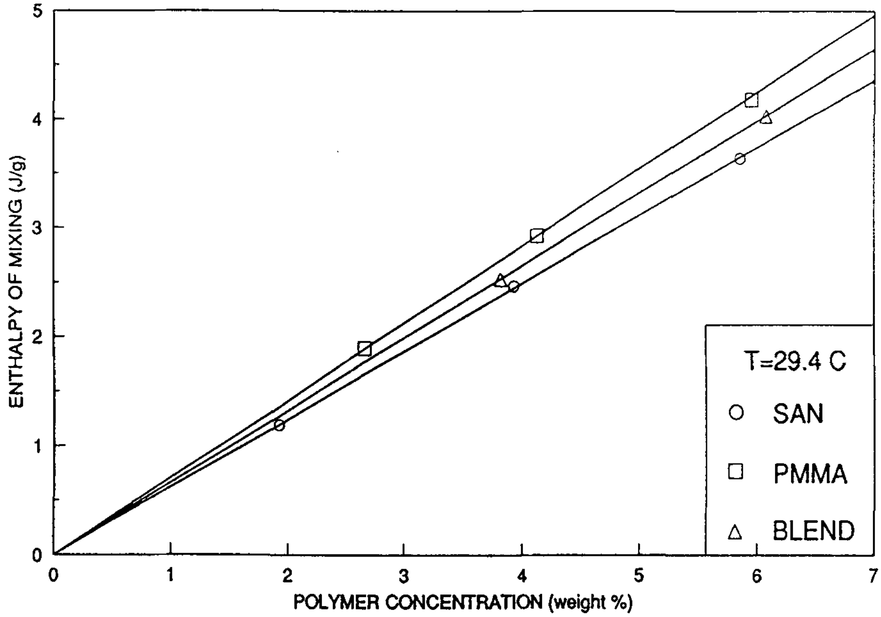

Fig. 1 Experimental enthalpies of mixing obtained at 29.4°C. Symbols: experimental data; lines: linear correlations (see Table 1)

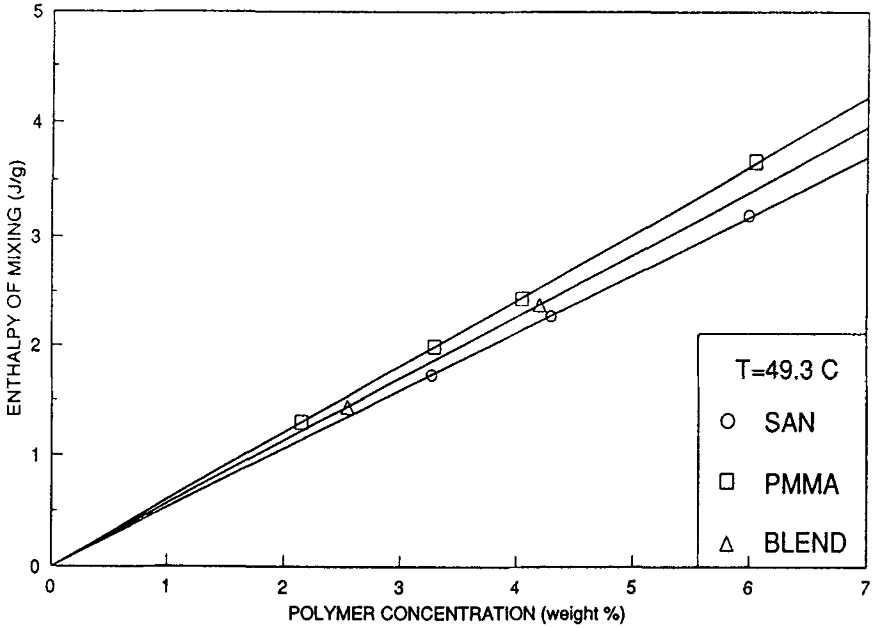

Fig. 2 Experimental enthalpies of mixing obtained at 49.3°C. Symbols: experimental data; lines: linear correlation (see Table 1)

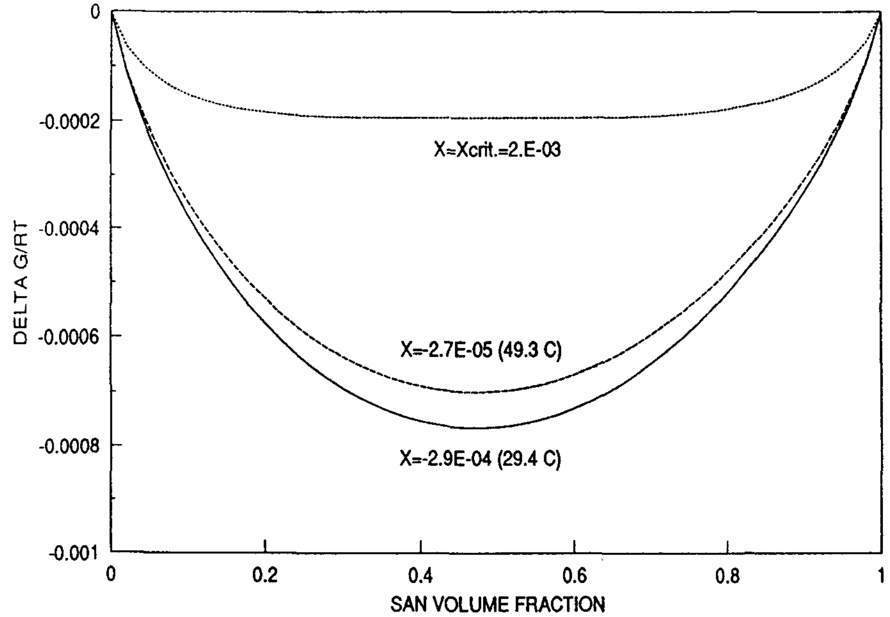

Fig. 3 Free energy of mixing behaviour for various $\chi_{(1,2)}$ values: χ critical and $\chi = f(T)$

These results support the conclusion that, in general, the entropy of mixing of SAN with PMMA is approximately zero, therefore the free energy of mixing and the compatibility between these two components is almost due to the enthalpy of mixing. Moreover the negative values for χ suggest that specific interactions between SAN and PMMA exist as one can easily realise from analysis of their chemical structures. Lastly, in Fig. 3, is showed $\chi_{(1,2)}$ *vs.* temperature and these curves give confirmation for a LCST type mixture behaviour.

Appendix

T = temperature /K
ΔH_{mix} = enthalpy of mixing
ΔG_{mix} = free energy mixing
ΔS_{mix} = entropy of mixing
$FH\chi_{(1,2)}$ = Flory-Huggins interaction parameter for the components 1 and 2
φ_i = volume fraction for component *i*
N_i = number of segment for polymer *i*
ΔH_i^{s} = experimental heat of solution for component *i*
$\Delta H_i^{\mathrm{blend}}$ = experimental heat of solution for blend
$\Delta H_{\mathrm{mix}(1,2)}$ = calculated heat of solution between component 1 and 2 by Hess Law

ρ = density / $g \cdot cm^{-3}$
PMMA = poly(methyl-methacrylate)
SAN = poly(styrene-co-acrylonitrile)
PTFE = poly(tetrafluoroethylene)
LCST = Lower Critical Solution Temperature
GPC = Gel Permeation Chromatography

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Zusammenfassung — Die unmittelbare Bestimmung der Mischungsenthalpie (ΔH_{mix}) ist für die Vorhersage der Mischbarkeit in Polymer-Polymer-Systemen von Interesse. Derartige Messungen verursachen operative Schwierigkeiten, weshalb der Versuch einer geeigneten indirekten Methode unternommen wurde. Die Mischungsenthalpie (ΔH_{mix}) wird durch die Anwendung des Hess'schen Satzes auf die Messung der Lösungswärme von Gemischen und ihrer Bestandteile in einem gewöhnlichen Lösungsmittel erhalten.

Für ein SAN/PMMA-Gemisch mit dem Gewichtsverhältnis 50:50 wurden die Experimente anhand der Hess'schen Näherung bei 29.4 und 49.3°C an verdünnten Lösungen durchgeführt und man erhielt für verschiedene Konzentrationen sehr gute Korrelationsangaben. Dies führt zu negativen Werten für den Wechselwirkungsparameter $FH\chi_{(1,2)}$ und anhand des ΔG_{mix}-Diagrammes ist es möglich, für jede Temperatur einen Vergleich bezüglich dem LCST-Verhalten dieser Gemische anzustellen.