Journal of Thermal Analysis, Vol. 33 (1988) 1079–1084

THE MEASUREMENT OF HEATS OF MIXING OF POLYMER ALLOYS BY A HEAT OF SOLUTION METHOD

P. N. Aukett and *C. S. Brown*

BP RESEARCH CENTRE, SUNBURY-ON-THAMES, MIDDLESEX, U.K.

Direct measurement of the heat of mixing (interaction) of polymers is not feasible due to their high viscosity. The indirect approach described here is a heat of solution method, in which a Hess's Law cycle is used to determine the heat of mixing from the individual heats of solution of the alloy and its constituent polymers in a common solvent. The main limitation of this approach lies in obtaining adequate precision on the experimentally determined heats of solution, as these are large compared to the calculated heat of mixing.

With this method the heat of mixing of a 75/25(%by wt) poly(dimethyl) phenylene oxide/polystyrene alloy has been determined by Setaram C-80 microcalorimeter as 4.9 + 0.2 Jg^{-1}. The precision of the method shows an improvement compared with published data.

Polymer have become increasingly important with the growth in the world market for performance polymers [1, 2]. There is a need for polymeric materials that posses a variety of special physical properties. This is not always possible to achieve with a single polymer, even when reinforced with glass or carbon fibre. The combination of properties offered by polymer alloys, sometimes exceeding that of either component polymer (e.g. high impact polystyrene [3, 4], in an attractive solution.

Metals form alloys because of an increase in entropy on mixing. In a system containing two polymers the effect of entropy is negligible and consequently most polymer pairs do not mix. The important factor in producing polymer alloys, is the degree of interaction between the polymers. In only a few cases, notably poly(dimethyl phenylene oxide)/polystyrene (PPO/PS) is this interaction sufficiently exothermic to promote miscibility. Direct measurement of the enthalpy of mixing (ΔH_m) is not feasible due to the high viscosity of polymers. Various indirect methods have, however, been published [5]. These include melting point depression, heats of solution, vapour sorption, inverse gas chromatography, small angle X-ray scattering, neutron scattering, and heat of mixing of low molecular weight analogues. The heat of solution method is the most promising [6] and is the subject of this paper.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

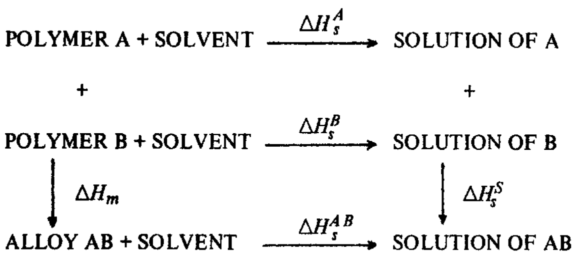
Heat of solution method

In the heat of solution method a Hess's law cycle is used to determine ΔH_m from the heats of solution (ΔH_s) of the alloy and its constituents in a common solvent [6, 7]. Figure 1 illustrates the cycle used to determine ΔH_m. Provided that the final concentration of the polymers is small (< 1 weight per cent [7], the heat of mixing of the two solutions of A and B, ΔH_s^S, can be neglected. Therefore for the general case:

$$\Delta H_m = a\Delta H_s^A + b\Delta H_s^B - \Delta H_s^{AB} \tag{1}$$

where a and b are the weight fractions of A and B in the alloy AB.

The experimentally determined heats of solution are large (ca 30–60 $\mathrm{Jg^{-1}}$) compared to the heat of mixing (ca 1–5 $\mathrm{Jg^{-1}}$). The main limitation of the Hess's law approach is therefore the difficulty in attaining adequate precision. At present it can only be used for alloys where there is a strong interaction between the components, i.e. where ΔH_m is large and negative. Heats of mixing for PPO/PS have been previously determined by Karasz and coworkers [6, 7] using a Hess's law cycle. PPO/PS was therefore chosen for further study to see if an improvement in precision was possible.



$$\Delta H_s^A + \Delta H_s^B + \Delta H_s^S = \Delta H_m + \Delta H_s^{AB}$$

Fig. 1 Hess's Law scheme used to calculate ΔH_m from the heats of the alloy and its constituent homopolymers [7]

Experimental

The PS ($\bar{M}_w$ 115000, $\bar{M}_w/\bar{M}_n < 1.05$) and the PPO ($\bar{M}_w$ 46400, $\bar{M}_n$ 17000, $\bar{M}_w/\bar{M}_n = 2.73$) were both secondary standards obtained from Polymer

Laboratories and Aldrich respectively. The alloy was prepared by dissolving the PS and PPO in 1,2-dichlorobenzene; the solvent being subsequently removed at room temperature under vacuum. The alloy was then annealed under vacuum for 10 minutes at 270°, before being quenched. In this way, a compatible homogeneous alloy of composition 75/25 weight per cent PPO/PS was prepared without degradation, or crystallisation of the PPO. This was verified using a Perkin Elmer DSC 2C. The midpoint of the glass transition (T_g) and the change in specific heat (ΔC_p) at the glass transition was determined for the alloy and the homopolymers.

The heat of solution in 1,2-dichlorobenzene of the homopolymers and the alloy at 29.9 ± 0.1° were determined using a Setaram C–80 microcalorimeter. Setaram reversal mixing cells were used; these have two compartments separated by a loose fitting lid (Figure 2). To prevent evaporation of the solvent from the cell, a potential source of baseline instability, great care was taken to ensure that the cell was tightly sealed using teflon o-rings.

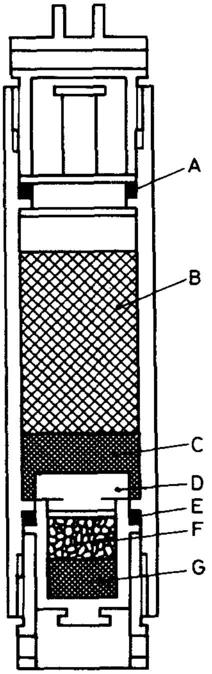


Fig. 2 Reversal mixing cell. A- O-ring seal, B-4.4 cm^3 1,2-dichlorobenzene, C-mercury, D-loose fitting lid, E- O-ring seal, F- ca 40 mg of polymer or alloy, G-mercury.

The calorimeter was inverted which caused the loose fitting lid to become detached, allowing the polymer or alloy to mix with the solvent. Continual inversion and re-inversion of the calorimeter stirred the contents. The rate of heat output was integrated using a Hewlett-Packard 86B microcomputer to obtain the total heat generated during solution.

Results and discussion

Seven determinations of the heat of solution were made for each material (Table 1). The arithmetic mean, the range, and the standard deviation from the mean are given. The reversal mixing facility on the C—80 enables both components to be pre-equilibrated at the set temperature of the calorimeter. Also, it was shown on a blank run that rotation of the calorimeter causes only minor disturbance (< 5 mJ) of the baseline, and therefore no correction needs to be made to the observed heat. These two factors taken together ensure a precision of < 0.5% relative standard deviation can be readily achieved for the determination of the heat of solution.

Table 1 – Heats of solution of homopolymers and alloy

Material	Heat of solution in 1,2-dichlorobenzene (Jg^{-1})		
	Mean	Range	σ
Polystyrene	25.9	±0.15	0.05
Poly(dimethyl phenylene oxide)	55.2	±0.3	0.1
PPO/PS 75%/25%	40.1	±0.45	0.2

As first noted by Karasz et al [6, 7], it is necessary to include a correction to ΔH_s to account for the glassy state of the polymers and the alloy. The correction term required to reduce the data to the liquid standard state is $-\Delta C_p \Delta T$. Where ΔC_p is the change in heat capacity at the glass transition temperature,. and ΔT is the difference between the glass transition temperature and the experimental temperature (29.9° in this case). These data are given in Table 2. The values are the mean of two determinations for the homopolymers, and four determinations for the alloy. The precision given is the range of results obtained.

Table 2 – Glass transition temperature and specific heat data measured by differential scanning calorimetry

Material	T_g, K	$-\Delta C_p$, Jdeg^{-1}g^{-1}	$-\Delta C_p \Delta T$, Jg^{-1}
Polystyrene	381 ±2	0.218 ±0.02	17.0 ±0.6
Poly(dimethyl phenylene oxide)	492 ±2	0.208 ±0.01	39.3 ±0.6
PPO/PS 75%/25%	450 ±2	0.222 ±0.02	32.6 ±0.8

For the PPO/PS 75/25 alloy the expression for calculating the heat of mixing, including the correction factor, is:

$$\begin{aligned}\Delta H_m &= 0.25\,\Delta H_s^{PS} + 0.75\,\Delta H_s^{PPO} - \Delta H_s^{PPO/PS} - 0.25\,\Delta C_p^{PS}\cdot\Delta T^{PS}\\ &\quad - 0.75\,\Delta C_p^{PPO}\cdot\Delta T^{PPO} + \Delta C_p^{PPO/PS}\,.\,\Delta T^{PPO/PS}\end{aligned} \tag{2}$$

This equation may be further simplified by assuming that the specific heat changes at T_g are additive. The data in Table 2 seem to indicate that this assumption is valid, i.e.:

$$\Delta C_p^{PPO/PS} = 0.25\,\Delta C_p^{PS} + 0.75\,\Delta C_p^{PPO}\ . \tag{3}$$

Equation (2) then becomes:

$$\begin{aligned}\Delta H_m &= 0.25\,\Delta H_s^{PS} + 0.75\,\Delta H_s^{PPO} - \Delta H_s^{PPO/PS} + 0.25\,\Delta C_p^{PS}\,(T_g^{PPO/PS} -\\ &\quad - T_g^{PS}) + 0.75\,\Delta C_p^{PPO}\,(T_g^{PPO/PS} - T_g^{PPO})\end{aligned} \tag{4}$$

This equation can be used to investigate the relative importance of the errors in each of the experimental measurements. If we consider the range in the measurements, which represent the maximum possible error, then the error due to the combined heats of solution is ± 0.7 Jg^{-1}. In contrast, the maximum possible error due to the combined DSC measurements of ΔC_p and T_g is only ± 0.05 Jg^{-1}. Therefore, it is the precision of the heat of solution measurement which is the limiting factor in applying this technique to polymer alloys with smaller heats of mixing than exhibited by PPO/PS.

Substituting the values from Tables 1 and 2 into equation (4) gives a value for the heat of mixing of –4.9 ± 0.2 Jg^{-1}. The precision is calculated using the standard deviations from the mean of the heat of solution measurements.

This assumes that the contribution of the DSC measurements to the error is negligible and that the measurements of the heat of solution are independent of each other. Karasz et al [6] determined a value of –4.4 ± ± 1.6 Jg^{-1} for a PPO/PS alloy containing 25 wt% PS. Within the given experimental error Karasz et al's result is consistent with the work described here. The error analysis carried out by these workers was an evaluation of the maximum possible error, taking into account the range of results obtained. Their error of ± 1.6 Jg^{-1} should therefore be compared to ± 0.7 Jg^{-1} in this work. A significant improvement in the precision of the method has therefore been obtained. This should allow many other polymer alloys to be studied.

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The permission of the British Petroleum Company plc to publish this paper is gratefully acknowledged. The authors would like to thank Professor Karasz for useful discussions.

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Zusammenfassung – Die direkte Messung der Mischungswärme (Wechselwirkungswärme) von Polymeren ist wegen ihrer hohen Viskosität nicht möglich. Die hier beschriebene indirekte Vorgehensweise beruht auf der Lösungswärme, wobei ein Hess'scher Kreisprozess verwendet wird, um aus den einzelnen Lösungswärmen der Mischung und der sie aufbauenden individuellen Komponenten im gleichen Lösungsmittel die Mischungswärme zu bestimmen. Die entscheidende methodische Grenze ist die notwendige Genauigkeit bei der Bestimmung der Lösungswärmen, da diese gross gegenüber der berechneten Mischungswärme sind.

Mit dieser Methode wurden die Mischungswärme einer Mischung aus 75% Poly(dimethylphenylenoxid) und 25% Polystyren in einem Mikrokalorimeter Setaram C 80 zu 4.9 ± 0.2 J g^{-1} bestimmt. Verglichen mit veröffentlichten Daten ist die Methode genauer.

РЕЗЮМЕ — Прямое измерение теплоты смешивания (взаимодействия) полимеров не представляется возможным из-за их высокой плотности. Описано непрямое приближение на основе метода измерения теплоты растворения, в котором используется закон цикла Хесса для определения теплоты смешения, исходя из каждой в отдельности теплот растворения полимерного сплава и составляющих его компонент в каком-либо общем растворителе. Основным ограничением этого приближения является получение адекватной точности экспериментально получаемых теплот растворения, поскольку они являются большими по сравнению с вычисленной теплотой смешивания. Исходя из этого метода и с помощью микрокалориметра Сетарам С—80 была определена теплота смешивания сплава полидиметилфениленоксида — полистирола с весовым соотношением 75 и 25 весовых %, равная 4,9 ± 0,2 дж$\cdot$г$^{-1}$. Точность метода была выше по сравнению с ранее опубликованными.