A study on polymer–polymer interactions through mixing calorimetry [1]

A. Brunacci [a], J. Yin [b], E. Pedemonte [c,*] and A. Turturro [c]

[a] *Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, Scotland, UK*

[b] *Changchun Institute of Applied Chemistry, Academia Sinica, Changchun 130022, People's Republic of China*

[c] *Istituto di Chimica Industriale, Università di Genova e Centro di Studi Chimico-Fisici di Macromolecole Sintetiche e Naturali, Corso Europa 30, 16132 Genoa, Italy*

Abstract

The aim of this work is to describe the most recent achievements in the field of the physical chemistry of mixing. The systems studied have been classified according to the amount of thermic effect due to the blending and its interpretation. When polystyrene (PS) and poly(α-methylstyrene) (PαMS) are blended, the interaction is weak and $\Delta_{mix}H$ is close to zero. The presence of polar atoms and/or groups increases the stability of the blend and, therefore, $\Delta_{mix}H$ becomes more negative. Poly(ethylene oxide) (PEO), poly-(methyl acrylate) (PMA), poly(methyl methacrylate) (PMMA) and poly(vinylacetate) (PVAc), when mixed to form binary systems, show large differences from their properties when pure. If hydrogen bonding takes place, the interactions are readily detected and a large effect is calorimetrically determined. Cellulose diacetate (CDA) and poly(vinylpyrrolidone) (PVP) have been studied as an example of a strongly interacting system.

INTRODUCTION

The needs of polymer science have led to a major contribution in the development of calorimetric techniques. DTA, DSC, TG, TMA and many other methods are widely applied in the study of homo- and copolymers and their blends. They provide rapid data and information on the sample probed. Nonetheless, polymer scientists need to investigate less immediate phenomena in order to understand and to model theoretically new materials, e.g. polymer alloys.

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* Corresponding author.

The degree of interaction between two different molecular chains or, more precisely, two different repeat units, is an important factor which helps to model not only the phase behaviour but also some physical properties of a blend. This quantity is associated with the enthalpy of mixing. While for low molecular-weight compounds the heat of mixing is directly detectable, in the case of polymers, their high viscosity does not allow its direct measurement. Hence, an alternative indirect technique is required to obtain this information.

The heat of solution method measures the heats of solution of a blend and its pure components in a suitable solvent, and the enthalpy of mixing is calculated from the appropriate Hess' cycle [1, 2]. In order to reduce the number of experiments, a modified version of this has been developed which measures the difference between the heats of solution of the blend ($\Delta_{sol}H^{B}$) and of a mechanical mixture of the two components ($\Delta_{sol}H^{1+2}$) of the same concentration and having the same composition. Figure 1 is a physical representation of this procedure for an exothermic example. This technique needs a correction, if measurements are performed below T_{g}, in order to obtain the enthalpy of mixing for the liquid state. The correction term is the enthalpy due to the conversion of the glasses into the hypothetical undercooled liquids. If the experiment temperature is lower than about $(T_{g} - 30)$ K, a direct calorimetric measurement of such a quantity is not possible and it must be calculated theoretically. The most suitable theory for this purpose, so far, is the Petrie–Marshall theory [3], because it requires data that are readily obtainable from a DSC
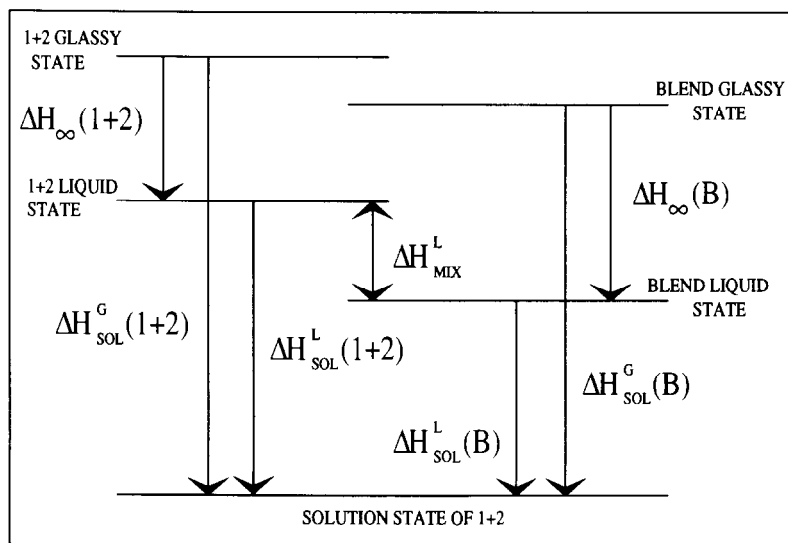

Fig. 1. Enthalpy level diagram for the cycle used to determine the $\Delta_{mix}H$ values of polymer blends: an exothermic example is shown.

experiment. The theory defines this value as the integral of the difference between the heat capacity of the glass and the heat capacity of the liquid extrapolated to the temperature required

$$\Delta_\infty H(T_a) = \int_{T_a}^{T_u} (C_{p_{glass}} - C_{p_{liquid}}) \, dT \tag{1}$$

The extremes of the integral are a generic upper temperature T_u, always above T_g, and the temperature T_a at which the glass is supposed to age. The overall enthalpy effect due to the glassy state contributions ($\Delta_{G \to L} H$) is evaluated by

$$\Delta_{G \to L} H = \Delta_\infty H^B - w_1 \Delta_\infty H^1 - w_2 \Delta_\infty H^2 \tag{2}$$

where w_i is the weight fraction of the ith component.

The systems examined were chosen in order to investigate not only the selected interactions but also the way in which the structure of the repeat unit changes the effects of mixing. It must be noted that, because the heats of mixing were measured at different temperatures so as to have the best experimental conditions, they are not strictly speaking equivalent. Nonetheless, a comparison of these results may be useful in order to indicate which criterion is the most powerful to obtain single-phase polymer blends.

EXPERIMENTAL METHOD AND MATERIALS

Some data concerning the polymers are listed in Table 1 which also, for simplicity, includes blending methods, solvents, and the temperatures at which the experiments were performed T_{exp}.

A Setaram C80 D calorimeter was used to determine heats of solution at a given temperature for each system. The thermostat precision is ± 0.001 K. Proper mixing during each single experiment was ensured by the calorimeter's ability to inverse its main body. Typically, solvent and samples were in contact after the first rotation.

Values of $\Delta_\infty H$ for the systems below their T_g values were calculated from C_p data. In the case of polystyrene (PS) and poly(α-methylstyrene) (PαMS), data were collected with a Perkin-Elmer DSC-2 using a sapphire sample as reference. Poly(vinylpyrrolidone) (PVP) and cellulose diacetate (CDA) were studied with a Mettler DSC using its internal reference, after having checked it with an indium sample. Although poly(methyl methacrylate) (PMMA) has a high T_g and poly(ethylene oxide) (PEO) is in the crystalline state, the temperature at which the calorimetric experiments were performed was chosen in order to avoid these unwanted physical states. Thus, their blends (see Table 1) with poly(methyl acrylate) (PMA) and poly(vinylacetate) (PVAc) were always in the liquid state.

The values of $\Delta_{G \to L} H$ shown in Table 2, were the calorimetric data of all

TABLE 1

Characteristic properties of the polymers and experimental conditions

Polymer	M_w/g mol^{-1}	M_w/M_n	Blending method	Calorimetric solvent	T_{exp}/K
PS	50000 [a]	<1.06 [a]	Cast by slow evaporation of		
PαMS	55000 [a]	<1.06 [a]	toluene solution	Toluene	333.1
CDA	59000 [b]	–	Cast from acetone/ethanol	Acetone/	
PVP	7400 [c]	1.52 [c]	(8:1) solution	ethanol (8:1)	297.5
PMA	30600 [c]	1.75 [c]	Cast from toluene		
PVAc	35000 [c]	2.00 [c]	solution	Toluene	333.1
PEO	24800 [a]	1.83 [a]	Cast from chloroform		
PVAc	41800 [c]	2.01 [c]	solution	Cyclohexanone	343.0
PMMA	174000 [a]	2.65 [a]	Freeze drying of benzene		
PEO	24800 [a]	1.83 [a]	solution	Cyclohexanone	397.6

[a] Nominal molecular weights. [b] Determination from intrinsic viscosity in acetone at 298 K.
[c] Characterized by GPC.

TABLE 2

Heats of solution and mixing, and glass effect corrections for the systems studied. The experimental uncertainty of these values is ± 0.5 J g^{-1}

System 1 + 2	(w_1/w_2)	$\Delta_{sol}H^{1+2}$/J g^{-1}	$\Delta_{sol}H^B$/J g^{-1}	$\Delta_{G\to L}H$/J g^{-1}	$\Delta_{mix}H$/J g^{-1}
PS + PαMS	(20/80)	−16.4	−7.4	−8.0	−1.0
	(50/50)	−9.2	−8.1	−0.2	−0.9
	(80/20)	−8.5	−7.3	−1.8	0.6
PEO + PVAc	(28/72)	16.9	21.4	–	−4.5
	(50/50)	16.8	20.1	–	−3.3
	(75/25)	16.0	18.4	–	−2.4
PMMA + PEO	(50/50)	−14.3	−15.7	–	−1.4
PMA + PVAc	(50/50)	14.8	32.6 [a]	–	−17.9 [a]
PVP + CDA	(10/90)	−38.3	−35.7	2.6	−5.2
	(35/65)	−35.5	−33.2	3.0	−5.3
	(60/40)	−26.0	−24.6	0.7	−2.1
	(85/15)	−22.2	−21.7	0.2	−0.7

[a] Experimental uncertainty is ± 0.9 J g^{-1}.

the systems are given, are not $\Delta_\infty H$ (see eqn. (2)), but represent the overall correction required by the $\Delta_{mix}H$ value in the glassy state to become the $\Delta_{mix}H$ value in the hypothetical undercooled liquid state. The blend compositions are expressed in weight fractions.

RESULTS AND DISCUSSION

It was assumed that PS and PαMS interact only very weakly because of the absence of polar groups and because of their similar structure [4]. From this theoretical point of view, it seems appropriate to consider these blends as energetically non-interacting. Hence, their enthalpies of mixing should be small, if not zero. This interpretation is supported by theoretical calculations made using the modified Guggenheim quasichemical model [5,6], which predicts a zero-effect upon mixing [7]. This model considers $\Delta_{mix}H$ values originating only from energies associated with the formation of i–j from i–i and j–j contacts, where i and j are groups present in the chain. Because the main side group is the same in both polymers, a non-zero $\Delta_{mix}H$ must have a different explanation. These contributions are usually called free volume [8] or liquid structure effects [9], for they are thought to rise from differences in volume properties, i.e. the thermal expansion coefficient α. As expected, these contributions are small and composition dependent. Figure 2 shows $\Delta_{mix}H$ values as functions of weight fraction for this system. However, the large experimental uncertainty, which is principally due to the difficulty of obtaining reliable heat capacity data for PαMS because of its tendency to depolymerize at temperatures above T_g, makes any interpretation rather questionable. According to Fig.
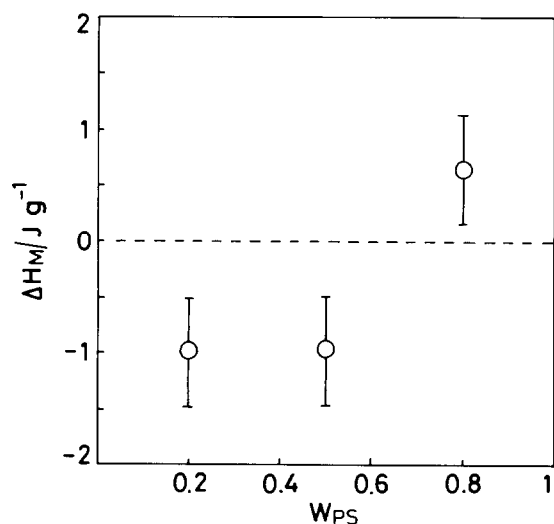

Fig. 2. $\Delta_{mix}H$ vs. weight fraction of PS for the system PS + PαMS.

2, PαMS does not fit the PS free-volume structures, and, hence, $\Delta_{mix}H$ is positive and unfavourable, although the blend is still single-phase. However, PS fits the PαMS structure well, its repeat unit having greater volume; thus $\Delta_{mix}H$ is negative and favourable. The miscibility limit shown by these two polymers [4] upon increasing the molecular weights may also be essentially due to these adverse contributions.

When polar atoms or groups are present in the repeat unit, some specific interaction may be established. The oxygen atom in the PEO repeat unit can act as a proton acceptor, whereas the carbon atom in the carbonyl group is positively charged and can be assumed to act in some way as a proton donor. Hence there is the possibility of polar–polar interactions in systems like PEO + PVAc, PEO + PMMA and PMA + PVAc.

Combining information from the calorimetric $\Delta_{mix}H$ values with other available data [10] for the PEO + PVAc system, a clear 'chemical' inter-action is detected [11]. From the shape of the $\Delta_{mix}H$ versus composi-tion curve in Fig. 3, it appears that interactions are maximized when one oxygen atom of PEO can interact with two carbonyl groups of PVAc, despite the steric hindrance due to the presence of the carbonyl oxygen. Decreasing the number of carbonyl groups, the number of interactions decreases, and the $\Delta_{mix}H$ value also decreases.

To investigate if a change in the structure of the repeat unit may significantly alter the $\Delta_{mix}H$ value, an experiment was performed on a 50/50 PEO + PMMA blend. The presence of a –CH$_3$ group in the chain does seem to impede these interactions [12], because the $\Delta_{mix}H$ value is less than half that of PEO + PVAc. Moreover, as shown in the PS and PαMS system, even a relatively small group such as –CH$_3$ can, to a certain extent,
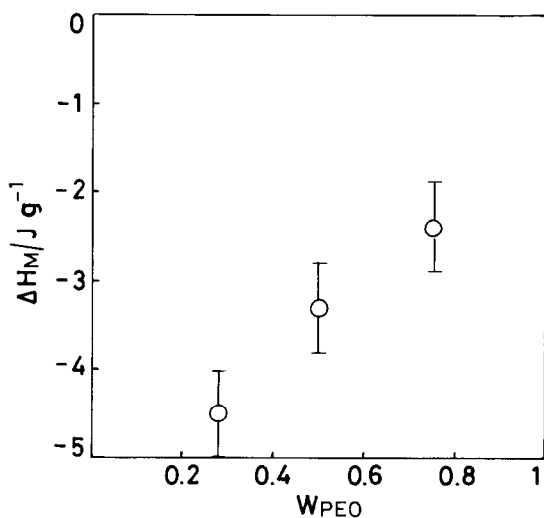

Fig. 3. $\Delta_{mix}H$ vs. weight fraction of PEO for the system PEO + PVAc.

lead to incompatibility and the free volume effect on the $\Delta_{mix}H$ value cannot be neglected. The chain flexibility of PMMA and of PVAc differ quite widely and, hence, it may be difficult to distinguish steric effects from free volume effects, although, in this comparison, it was assumed that differences between PVAc and PMMA carbonyl groups are negligible.

The assumption that free-volume contributions may play a significant role in the heats of mixing may be proved by the astonishingly exothermic heat of mixing of the 50/50 PMA + PVAc blend. These two polymers are the most similar of those studied in this work. The repeat units are isomers and their T_g values differ by only 50 K. FT–IR analysis [13] confirms qualitatively that interactions are centred on the side groups, but they do not imply such a large thermal effect. Liquid structure investigations [13, 14] on pure components and the blend suggest that better side-group packing is established after mixing. It appears that in this system the two effects—energy interaction and free volume—result in the blend having an extremely high degree of compatibility.

Specific interactions by hydrogen bonds can take place between PVP and CDA through their hydroxy and carbonyl groups. These interactions are easily detected by FT–IR and can be determined quantitatively by the study of $\Delta_{mix}H$ values as functions of composition (see Fig. 4). The strongest interaction seems to occur in the composition range between PVP/CDA = 15/85 and 30/70, where both PVP and CDA have almost the same number of moles of hydroxy and carbonyl groups (the exact composition is PVP/CDA = 17/83) and the chances of forming hydrogen bonds are maximized. Similar behaviour was observed for T_g and mechanical properties [15]. The $\Delta_{mix}H$ values decrease quite rapidly when
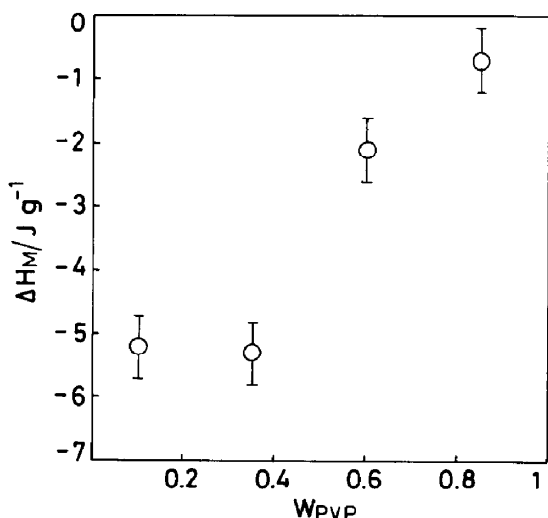

Fig. 4. $\Delta_{mix}H$ vs. weight fraction of PVP for the system PVP + CDA.

the PVP fraction is increased. This may be due to self-associated hydrogen bonding which gives a zero contribution to the heat of mixing.

CONCLUSIONS

Mixing calorimetry has shown great potential in the study of polymer–polymer interactions and of the thermodynamics of mixing. Although there are limitations for those systems which interact weakly, this technique may become very helpful in understanding blend properties as a function of their compositions. Moreover, it has been confirmed that it is no longer an acceptable approximation to predict polymer miscibility on a purely energetic basis, i.e. using the solubility parameter approach. The free volume contributions can substantially modify the blend properties, even when favourable interactions occur.

Further studies are required to evaluate the effects of different structures and the quantity of favourable interactions required to compensate free volume effects for better tailor-made physical properties of blends.

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