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HEAT OF MIXING IN POLYMER BLENDS BASED ON POLY(VINYL ACETATE)

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Abstract

Knowledge of the heat of mixing is very important in order to evaluate the interaction parameter, according to the Patterson theory. In this work we illustrate the results regarding some polymer blends, based on poly(vinyl acetate) and some polyacrylates with different substituent groups. In this way it is possible to understand the effect of the lateral group hindrance, as it will be illustrated in the paper.

Keywords: heat of mixing, polymer blends, poly(vinyl acetate)

Introduction

According to the Second Lay of Thermodynamics, two liquids will blend if the Gibbs free energy of mixing, ΔG_M, is negative. Since:

$$\Delta G_M = \Delta H_M - T\Delta S_M \tag{1}$$

ΔG_M will be negative if the entropy of mixing, ΔS_M, is positive and the enthalpy of mixing, ΔH_M, is negative or positive but small.

The combinatorial entropy of mixing [1] can be expressed as:

$$\Delta S_M/RV = -[(\varphi_1 \ln \varphi_1/\overline{V}_1) + (\varphi_2 \ln \varphi_2/\overline{V}_2)] \tag{2}$$

where R is the Gas Constant, V the total volume, φ_i the volume fractions of the components of the mixture and $\overline{V}_i$ the molar volumes of the pure components. Since $\varphi_i<1$, the entropy of mixing is positive, as required.

For blends of two polymers of high molecular weight, $\overline{V}_1$ and $\overline{V}_2$ are very high so that the two terms in Eq. (2) are very small and the entropic stabilization is vanished; the negative value of ΔG_M required for mutual solubility can only derive from the interaction contribution, expressed as ΔH_M. ΔH_M which will be positive and unfavourable to mixing if the two components interact through dispersion forces or random dipole-induced dipole interactions. ΔH_M

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will be negative and favourable to mixing if the two components interact through specific interactions, such as charge transfer or hydrogen bonding.

Knowledge of the heat of mixing, ΔH_M, is very important, because it is related to X_{12} [2, 3]:

$$X_{12} = \frac{\tilde{v}}{m_1 v_1^* \theta_2}[\Delta H_M - m_1 v_1^* p_1^* (\tilde{v}_1^{-1} - \tilde{v}^{+1}) - m_2 v_2^* p_2^* (\tilde{v}_2^{+1} - \tilde{v}^{-1})] \tag{3}$$

which is necessary to estimate the interaction parameter, χ_{12}, according to the theory of Patterson [4], which represents a quantitative evaluation of the miscibility of two polymers.

There are several ways of obtaining an estimate of the interactions between two polymers. However, a direct measurement of the heat of mixing is not possible, due to the very small heat effect involved and to the slow interdiffusion of the components. The more suitable indirect method consists in following a thermodynamic cycle based on the Hess's law:

$$\begin{tikzcd}
\text{Polymer 1} \arrow[d, "+\text{Solvent}"', "\Delta H_1"] & + & \text{Polymer 2} \arrow[r, "\Delta H_{mix}"] \arrow[d, "+\text{Solvent}"', "\Delta H_2"] & \text{Mixture (1+2)} \arrow[d, "+\text{Solvent}"', "\Delta H_4"] \\
\text{Solution 1} & + & \text{Solution 2} \arrow[r, "\Delta H_3"] & \text{Solution (1+2)}
\end{tikzcd}$$

Consequently, one needs to measure the heats of solution of the two pure polymers and of their blend in a common solvent, and ΔH_{mix} is calculated from:

$$\Delta H_{mix} = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 \tag{4}$$

Practically this method is not particularly successful, due to accumulation of errors in the four sets of experiments involved. In order to bypass this problem, it is more convenient to follow a cycle of this kind:

$$\begin{tikzcd}
\text{Polymer 1} & + & \text{Polymer 2} \arrow[rr, "\Delta H_{mix}"] \arrow[dr, "+\text{Solvent}"', "\Delta H_5"] & & \text{Mixture (1+2)} \arrow[dl, "+\text{Solvent}"', "\Delta H_4"] \\
& & & \text{Solution (1+2)} &
\end{tikzcd}$$

so that:

$$\Delta H_{mix} = \Delta H_5 - \Delta H_4 \tag{5}$$

where ΔH_5 is the heat of dissolution of the 'mechanical mixture' an ΔH_4 is the heat of dissolution of the 'chemical blend'. The error is diminished since the number of experiments is reduced.

Table 1 Characteristics of the samples used in the experiments

Samples	M_n/g mol^{-1}	q	T_g/K
PVAc	52700	2.37	306
PMA	17500	1.75	271
PEA	29200	2.45	257
PBA	–	–	228

Materials and techniques

In our work we have studied several systems based on poly(vinyl acetate), PVAc, mixed with some polyacrylates, having different substituent groups. In particular we have examined the mixtures poly(vinyl acetate)–(poly(methyl acrylate), (PVAc–PMA), poly(vinyl acetate)–poly(ethyl acrylate), (PVAc–PEA), and poly(vinyl acetate)–poly(butyl acrylate), (PVAc–PBA). The charac- teristics of the samples used are listed in Table 1.

The heat of solution measurements were carried out with a SETARAM C80D calorimeter, using cyclohexanone as common solvent at a temperature of 333±0.1 K, so that all the polymers were in the liquid state. A reversal mixing equipment was adopted in order to improve the dissolution speed.

According to the recommended procedure, the sample was placed in the lower container of the measuring cell and the solvent in the upper one (see Fig. 1). A mercury seal and a lip were used to separate the two containers and

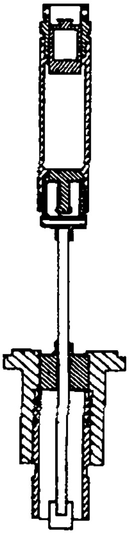

Fig. 1 Measuring vessel

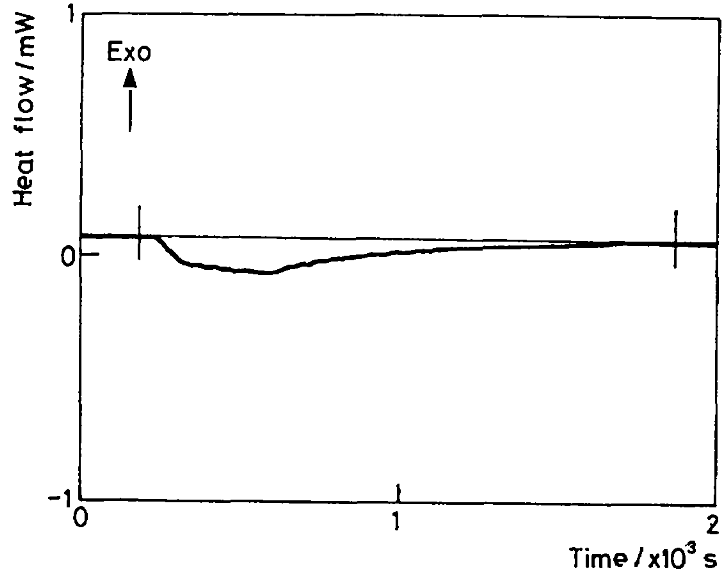

Fig. 2 An example of the dissolution curve

Table 2 Heats of mixing, ΔH_M, of different mixtures

Mixture	PMA/PVAc 50/50	PEA/PVAc 25/75	PEA/PVAc 75/25	PBA/PVAc 25/75
ΔH_M/mJ mg^{-1}	–0.5	-1.8	3.7	0.8

the same quantities of solvent and mercury were placed in the reference vessel. Sample mass and solvent volume were established to obtain final concentrations of less than 0.2%w/v.

In Fig. 2 we present an example of dissolution curve, with the integration limits and the base line.

The heats of solution listed in Table 2 were calculated by means of the least squares method applied on the straight lines obtained for the heat of solution, expressed in mJ, as function of the sample mass, expressed in mg (Fig. 3). In such a way the heat of solution measurements were effected with an error of less than 5%.

Results and discussion

This work is part of a wide study in order to understand the effect of different parameters on polymer miscibility (i.e. molecular weight, functionalization, temperature, composition, steric hindrance and so on). Here we have stud-

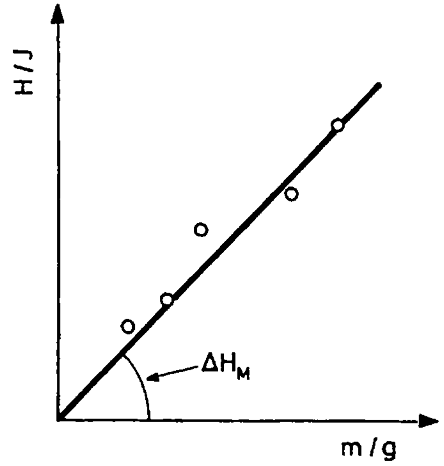

Fig. 3 Interpolation of the experimental points for the evaluation of the heat of mixing by the least sqares method

ied in particular the effect of the steric hindrance of the lateral groups on the miscibility of two polymers.

For the mixture PVAc–PMA [5, 6], it can be foreseen that the solubility is high due both to the combinatorial entropy of mixing and to the interactions between similar but polar groups. Actually the miscibility strongly depends on the molecular weight of the components; in a previous work [7], with PVAc samples of lower molecular weight, a quite large and negative heat of mixing has been measured. In our case, the heat of mixing is practically zero, so that miscibility seems to be due mainly to the combinatorial entropy of mixing.

The results obtained for the PEA–PVAc mixture [8] show that the process of mixing is slightly exothermic only for the composition 25/75; it is evidently endothermic for the composition 50/50 and 75/25. This means that the high hindrance of the ethyl group does not allow a sufficient number of interactions, so that miscibility is possible only with smaller amounts of PEA. In addition, these results indicate a composition-dependent miscibility not accounted for in the simplified Patterson's theoretical treatment, but in line with the expectations from the equation of state theory.

Finally, for the PBA–PVAc 25/75 mixture, the heat of mixing is close to zero and the process of mixing does not produce significant enthalpic effect. We can conclude that a small of PBA is sufficient compared with the mixture PEA–PVAc, to prevent favourable interactions between polymer chains.

We underline, nevertheless, that it is not easy to compare these results because PMA, PEA and PBA have different molecular weights and the process of mixing is strongly influence by this parameter.

Conclusions

These results show that addition of bulky lateral groups in the main chain, such as EA and BA compared with MA, makes the system less miscible. This fact can be explained by considering the increasing steric hindrance of the lateral groups, proceeding from MA to EA and finally to BA. Therefore we can conclude that the hindrance of the lateral groups is one of the most important and critical factors in the process of mixing between two polymers.

The effect of this parameter is similar to that of the molecular weight, studied in another work [5]. In that case we have shown that an increase in the molecular weight causes a decrease in miscibility, due to the decrease in the free volume. A similar argument can be applied to this case. An increasing hindrance of the lateral groups causes a decrease in free volume and a subsequent increase in density, so that the polymer chains encounter increasing difficulties in interacting with each other.

Finally, we must underline some inconsistencies between theory and experiments; we have found, in particular, a composition dependence in miscibility, which is not considered in Patterson's theoretical treatment. This fact confirms that approximations, adopted by Patterson, in order to simplify calculations, cause some errors, which be reduced only be developing less approximated and more rigorous theoretical models. In this way calculations become more complicated, but the results are probably more reliable.

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