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Study on miscibility of PEO and PCL in blends with PHB by solution viscometry

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Abstract

Viscometric studies were carried out for polymer-blend solutions in chloroform, i.e. for solutions of two polymers in a common solvent. Polymer blends comprised poly(3-hydroxy butyrate) (PHB) in combination with poly(ethylene oxide) (PEO) and poly(ε-caprolactone) (PCL), respectively. Experimental results obey the Huggins equation to an excellent approximation in the concentration range studied. Intrinsic viscosities vary linearly with blend composition to a good approximation. Huggins coefficients display generally nonlinear dependencies on blend composition. Positive deviations from perfect behaviour are attributed to attractions between different chain molecules or miscibility of the constituents. The viscometric study demonstrates that PEO is miscible with PHB, whereas PCL is immiscible.

Keywords: Polymer blends; Solution viscometry; Poly(3-hydroxy butyrate)

1. Introduction

We report on the viscosity of ternary polymer-blend solutions to reveal dominant interactions in polymer blends. Knowledge about interactions between constituents in polymer blends is important for the understanding of their phase behaviour. The viscometric method utilises the fact that polymer–polymer interactions are reflected in the viscosity of polymer-blend solutions consisting of polymers A and B in a common solvent. In recent years, several attempts have been made using dilute-solution viscometry to predict polymer–polymer miscibility [1–12]. For instance, miscibility of poly(vinyl chloride) with poly(ε-caprolactone) (PCL), poly(ethylene oxide) (PEO) and polystyrene, respectively, was studied in Refs. [9–11]. Evaluation of polymer–polymer miscibility is especially complicated in polymer blends comprising crystallisable constituents. Solution viscometry is then a powerful tool in assessing the miscibility of the components in the amorphous state.

Starting point is the equation for the viscosity of a polymer solution proposed by Huggins [13]. According to Huggins' equation, the second-order term in the viscosity as a function of polymer concentration represents interactions between constituents of the system. This equation is extended to a polymer-blend solution consisting of two polymers in a common solvent. There are polymer–solvent and polymer–polymer interactions in the system. The interactions, including polymer–polymer interactions, are reflected in Huggins' equation via hydrodynamic interactions. In a common solvent, coils have a certain hydrodynamic volume. This volume will change owing to attractions or repulsions between chemically different chains, which in turn causes the alteration of the Huggins coefficient. It means that we can deduce information about polymer–polymer interactions from the Huggins coefficient. Given the two polymers are dissolved in a common good solvent. At sufficiently low concentrations of polymer, they form separate swollen coils that behave like hard spheres and do not interpenetrate. Hence, one expects additive behaviour of intrinsic viscosities in ternary solutions. When the concentration increases, the coils will interpenetrate and the Huggins coefficient reflects not only polymer–solvent but also polymer–polymer interactions. In this way, one can determine easily parameters from measurements of viscosity that are suitable to evaluate the phase behaviour of a polymer blend.

In the present study, we focus on polymer–polymer interactions between poly(3-hydroxy butyrate) (PHB) and PEO as well as between PHB and PCL as extracted from the viscosities of blend solutions in chloroform. Viscosity

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data, obtained by Ubbelohde viscometry, are examined in terms of Huggins' equation. This analysis leads to suitable parameters that can be used to characterise the phase behaviour of polymer blends. The main objective is the evaluation of the miscibility or immiscibility in blends of PHB with PEO and PCL, respectively, in terms of these parameters.

2. Theoretical background

We start with Huggins' equation for the viscosity of polymer solutions. Formulated for a polymer-blend solution, it reads

$$\eta_{\mathrm{spec,b}} = [\eta]_{\mathrm{b}}c_{\mathrm{b}} + K_{\mathrm{b}}[\eta]_{\mathrm{b}}^2c_{\mathrm{b}}^2 \tag{1}$$

where c is the mass concentration of the macromolecules in the solvent and K is the Huggins coefficient. Subscript b refers to polymer blend. Specific viscosity, η_{spec}, and intrinsic viscosity, $[\eta]$, are defined as usual. Quantity $[\eta]$ of Eq. (1) comprises the dependence of the terms on molecular mass. Hence, the Huggins coefficient is independent of molecular mass to a good approximation.

Eq. (1) provides a linear relationship between reduced viscosity, η_{spec}/c, and concentration c with intercept $[\eta]$, and the slope yields the dimensionless Huggins coefficient K. Quantities $[\eta]_{\mathrm{b}}$ and K_{b} that follow from Eq. (1) refer to the blend solution. For convenience, we express quantities in Eq. (1), that concern the blend, as superposition of constituents' properties. Total polymer concentration, c_{b}, and intrinsic viscosity of the perfect blend solution, $[\eta]_{\mathrm{b},id}$, are introduced as follows:

$$c_{\mathrm{b}} = c_1 + c_2 \qquad [\eta]_{\mathrm{b},id}c_{\mathrm{b}} = [\eta]_1c_1 + [\eta]_2c_2 \tag{2}$$

As mentioned before, the second equation of Eq. (2) is straightforward since one expects additivity of the intrinsic viscosities for dilute solutions. We may also introduce the mass fraction of polymer component 1, it is

$$w = \frac{m_1}{m_1 + m_2} = \frac{c_1}{c_{\mathrm{b}}} \tag{3}$$

Using the superpositions introduced in Eq. (2), the second term of Eq. (1) may be expressed as follows by the individual concentrations and intrinsic viscosities of the constituents:

$$K_{\mathrm{b}}[\eta]_{\mathrm{b},id}^2c_{\mathrm{b}}^2 = K_1[\eta]_1^2c_1^2 + K_2[\eta]_2^2c_2^2 + 2K_{12}[\eta]_1[\eta]_2c_1c_2 \tag{4}$$

The ideal solution of components 1 and 2 is defined in terms of intrinsic viscosities according to Eq. (2). We add here a definition in terms of Huggins coefficient K. A solution is defined as ideal if the second-order term of Eq. (1) also behaves additively, i.e. the coefficient K_{12} of Eq. (4) reads

$$K_{12} = (K_1K_2)^{1/2} \tag{5}$$

Eq. (5) allows the separation of the experimental Huggins coefficient, K_{b}, in two parts: the Huggins coefficient of the perfect solution, K_{id}, and the excess quantity ΔK

$$K_{\mathrm{b}} = K_{id} + \Delta K \tag{6}$$

To simplify the notation, we introduce the parameter α as follows:

$$\alpha = \frac{[\eta]_1}{[\eta]_2} \tag{7}$$

Quantity α represents the ratio of sizes of the macromolecules under discussion. Using Eqs. (3)–(5) and (7), the ideal Huggins coefficient, K_{id}, and the excess quantity, ΔK, read as follows:

$$K_{id} = \left(\frac{\sqrt{K_1}\alpha w + \sqrt{K_2}(1 - w)}{1 + (\alpha - 1)w}\right)^2 \tag{8}$$

$$\Delta K = 2\frac{w(1 - w)\alpha}{(1 + (\alpha - 1)w)^2}\kappa \qquad \text{with } \kappa \equiv [K_{12} - (K_1K_2)^{1/2}] \tag{9}$$

The experimental excess quantity ΔK_{exp} follows from Eq. (6) with Eq. (8). It reveals deviations from ideal behaviour that are, to a good approximation, chiefly due to thermodynamic interactions between the different macromolecular species. At sufficiently high polymer concentration, coils will interpenetrate. Attractions between chemically different molecules will then cause swelling of the coils leading to an excess increase in viscosity as compared to perfect behaviour. Hence, positive deviations from ideal behaviour are indicative of attractions between the different polymer species, whereas negative deviations result from repulsions. Expressing these findings in terms of coefficient κ, it follows

$$\kappa > 0\text{—miscibility} \tag{10}$$

and

$$\kappa < 0\text{—immiscibility} \tag{11}$$

The coefficient κ, introduced in Eq. (9), has to be determined for a certain blend by a least-square procedure using all experimental values $\Delta K_{\mathrm{exp},i}$ for different blend compositions w_i. Denoting in Eq. (9) the factor in front of κ by q, the best value for κ follows from

$$\sum_{i=1}^{n}[\Delta K_{\mathrm{exp},i} - \kappa q_i]^2 = \min \tag{12}$$

where n is the number of experimental data points available over the composition range given by w_i. The more data points for different blend compositions we have the more precise is the determination of coefficient κ.

3. Experimental

3.1. Materials

Polymers used in this study were purchased from

Table 1
Polymer specifications

Polymer	M_w	(M_w/M_n)	Source
PCL	80,000	1.95	Union carbide
PEO	100,000	1.91	Acros
PHB (1)	120,000	2.03	Aldrich
PHB (2)	550,000	2.5	Aldrich

different sources. Especially, two different samples of PHB, having different molecular masses, were applied. Details are summarised in Table 1. Polymers were purified by dissolution and precipitation in chloroform and methanol, respectively, and finally dried in vacuum at 50 °C for 48 h. Chloroform, used as solvent, was obtained from Merck.

3.2. Viscosity measurement

Ternary solutions of PEO and PCL, respectively, with PHB were prepared by dissolving polymer mixtures having different weight ratios in chloroform at 50 °C. The solutions were diluted to the designated volume at room temperature to correct the concentrations. Purification of solutions was done by filtration using nylon membrane filter prior to viscosity measurement.

Ubbelohde viscometers of appropriate sizes were employed to determine the relative viscosities, η_r, of the blend solutions. In any case, the flow time of pure solvent exceeded 200 s so as to minimise experimental errors. Values of η_r fall within the range of 1.2–2.0. Under these experimental conditions, the kinetic energy and shear corrections were negligible. Viscosity measurements were carried out at 298 K. Temperature control was recorded to ±0.1 K.

4. Results and discussion

4.1. Viscosities

Plots of specific viscosity over blend concentration, η_{spec}/c, versus concentration c, for blend solutions of PHB with PEO and PCL, respectively, are shown in Fig. 1. Data for all systems fit Huggins equation (1) with high correlation; typically, correlation coefficients amount to $r = 0.9998$. Selected results for intrinsic viscosities and Huggins coefficients are compiled in Table 2. We note that both PCL and PEO display higher intrinsic viscosities than that of PHB (1). If one approximates intrinsic viscosity by the ratio of hydrodynamic volume and molecular mass, V_h/M, one may estimate the ratio of hydrodynamic volumes. Using the data of Tables 1 and 2, it follows

$$\frac{V_{h,PEO}}{V_{h,PHB(1)}} = 1.6 \quad \text{and} \quad \frac{V_{h,PCL}}{V_{h,PHB(1)}} = 1.5 \tag{13}$$

The ratios of hydrodynamic volumes are not very different for the two parent polymers of the blends.

Intrinsic viscosities, $[\eta]$, versus blend composition are depicted in Fig. 2 for PHB in blends with PEO and PCL, respectively. Regression analysis shows that intrinsic viscosities, obtained from Fig. 1 by extrapolation to zero concentration, have errors of around 0.2% (cf. Table 2). Therefore, error bars are too small to be drawn in Fig. 2. It becomes obvious that intrinsic viscosities for blends of PEO and PHB obey linear relationships with respect to blend composition as given by Eq. (2) to an excellent approximation (see Fig. 2a). For blends of PHB and PCL, minor negative deviations from additivity can be recognised. These deviations exceed experimental errors and might be indicative of slight shrinkage of the coils owing to different quality of the solvents for the polymer species in the ternary solution. Since in terms of Eq. (6), Huggins

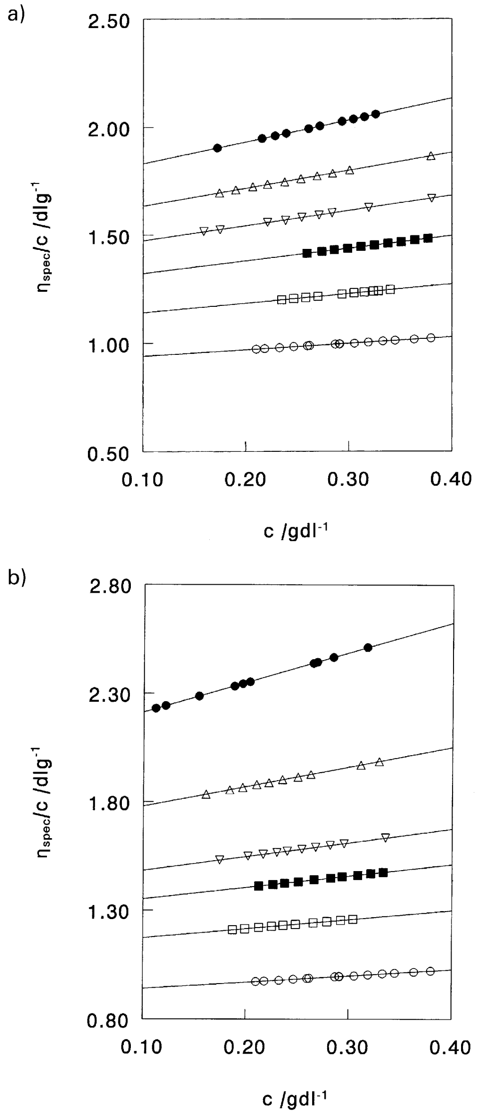

Fig. 1. Solution viscosity η_{spec}/c versus blend concentration, c, for blend solutions in chloroform at 298 K. Blend compositions, X/PHB (X = PEO,PCL), (●) 100/0, (△) 80/20, (▽) 50/50, (■) 40/60, (□) 20/80, (○) 0/100. (a) Blends of PEO and PHB (1); (b) blends of PCL and PHB (1).

Table 2
Selected intrinsic viscosities and Huggins coefficients for blends with PHB

Sample	$[\eta]$ ($\mathrm{cm}^3\ \mathrm{g}^{-1}$)	K	K_{id}
PEO/PHB (1)			
100/0	173.2 ± 0.2	0.3347 ± 0.0035	
70/30	151.1 ± 0.2	0.3451 ± 0.0045	0.3373
50/50	140.4 ± 0.4	0.3529 ± 0.0092	0.3395
30/70	112.5 ± 0.4	0.364 ± 0.013	0.3424
0/100	91.2 ± 0.2	0.3487 ± 0.0082	
PEO/PHB (2)			
70/30	205.7 ± 0.6	0.3618 ± 0.0076	0.3389
50/50	234.7 ± 0.3	0.3526 ± 0.0046	0.3409
30/70	264.5 ± 0.6	0.3493 ± 0.0070	0.3426
0/100	295.0 ± 0.7	0.3446 ± 0.0054	
PCL/PHB (1)			
100/0	207.6 ± 0.2	0.3180 ± 0.0033	
70/30	162.3 ± 0.3	0.3146 ± 0.0065	0.3228
50/50	142.2 ± 0.2	0.3131 ± 0.0043	0.3272
10/90	102.5 ± 0.2	0.3349 ± 0.0091	0.3424

coefficient K_{b} only depends on ratio α, Eq. (7), the deviations are neglected in what follows.

4.2. Huggins coefficients

Experimental values of the Huggins coefficients for pure components, K_1 and K_2, and for blends, K_{b}, were determined according to Eq. (1) from the slopes of the functions presented in Fig. 1. A few results are listed in Table 2. Values of K_{id} were calculated after Eq. (8). Optical inspection of the data in Table 2 shows that we observe outside experimental errors

$\Delta K > 0$ for PEO/PHB blends

and

$\Delta K < 0$ for PCL in blends with PHB.

These results indicate miscibility of the two constituents in blends of PHB and PEO whereas immiscibility in blends with PCL. Comparison of the data for PHB (1) and PHB (2) shows that the result does not depend on the molecular mass of the polymers. This can be seen more clearly in Fig. 3a–c where experimental values of K_{b} are depicted versus blend composition. Positive and negative deviations from ideal behaviour become evident. Relevant results are summarised in Table 3. Parameters κ are the result of regression calculations according to Eq. (12). Table 3 and Fig. 3a and b demonstrate that values for quantities κ and K_{12} do not depend on molecular mass to a very good approximation. For the blend PEO/PHB, it becomes obvious that the value of K_{12} exceeds significantly the values of K_i for the parent constituents. The opposite is true for blends of PCL and PHB. This fact points towards miscibility of the components in the former case and immiscibility in the latter case. These conclusions are consistent with results published in Refs. [14–16]. Martuscelli et al. inferred miscibility of PHB and PEO from melting point depression [14]. Measurements of glass transition temperatures supported this conclusion [15]. On the other hand, detection of glass transition temperatures and morphological studies provided evidence for immiscibility of PHB and PCL [16].

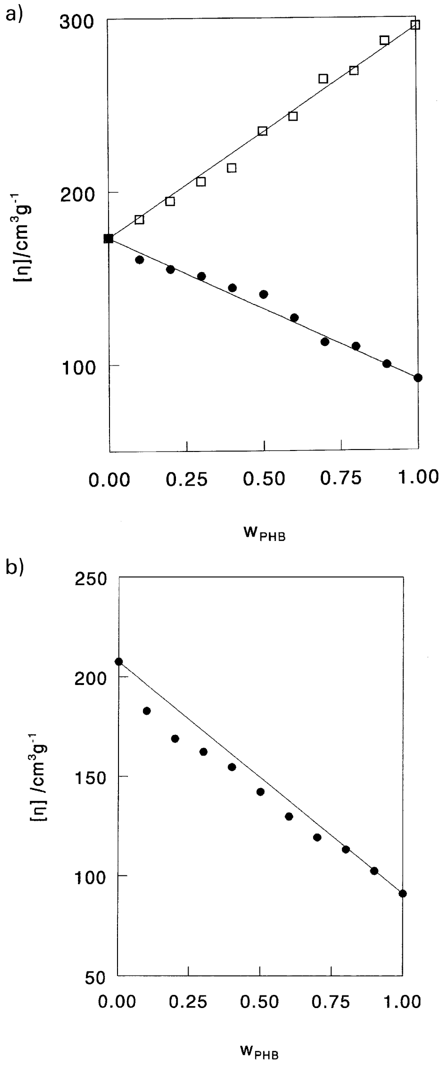

Fig. 2. Intrinsic viscosity as a function of PHB weight fraction in different blends. The solid curves were calculated according to Eq. (2). (a) PEO/PHB blends: (●) PHB (1), (□) PHB (2); (b) PCL/PHB (1) blends.

One easily verifies that Huggins coefficient $K_{\mathrm{b}}(w)$ of Eq. (6), with Eqs. (8) and (9), has an extreme value with respect to composition w_1 at

$$\frac{1}{w_1} = 1 + \left(\frac{K_1 - K_{12}}{K_2 - K_{12}}\right)\alpha_1 \tag{14}$$

Figs. 3a–c shows that the extreme values of the regression curves agree fairly with experimental results.

5. Conclusions

Viscometric studies on polymer-blend solutions of PHB

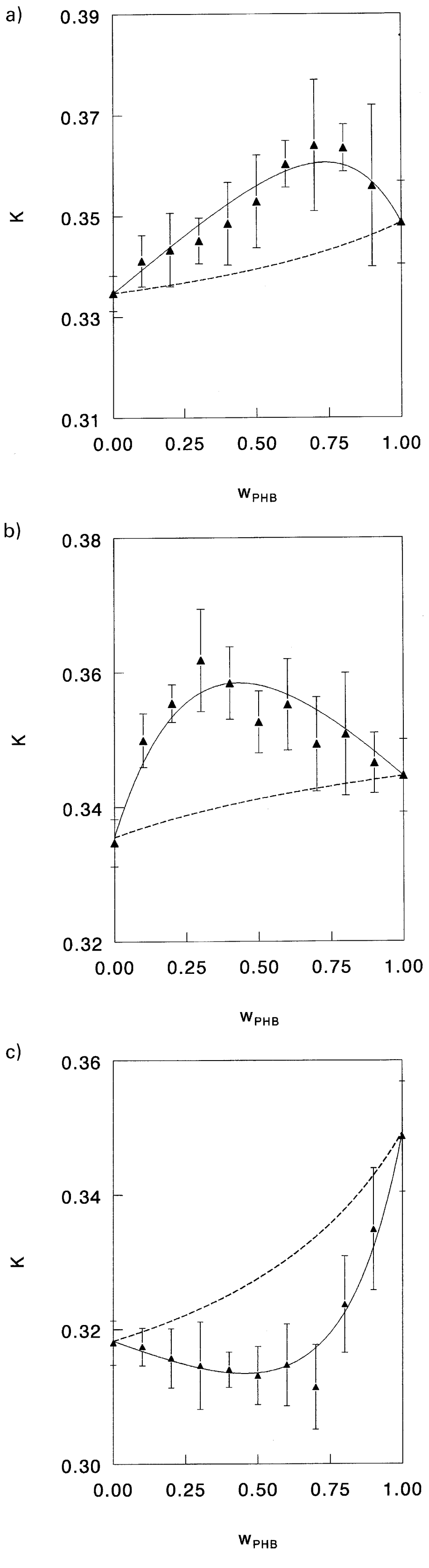

Fig. 3. Huggins coefficient versus blend composition. The dashed curve represents perfect behaviour according to Eq. (8), the solid curve is the regression curve according to Eqs. (9) and (12). (a) PEO/PHB (1), (b) PEO/PHB (2), (c) PCL/PHB (1).

Table 3
Huggins coefficients, parameter κ and extreme value of function $K(w)$ for the blends

System	K	K_{12}	κ	$w_{\mathrm{PHB}}^{\mathrm{extr}}$
PEO	0.335			
PCL	0.318			
PHB (1)	0.349			
PHB (2)	0.345			
PEO/PHB (1)		0.378	0.037	0.738
PEO/PHB (2)		0.376	0.036	0.437
PCL/PHB		0.300	−0.033	0.457

with PEO and PCL, respectively, in chloroform demonstrate that the Huggins equation is valid to an excellent approximation in the range of blend concentrations studied. Intrinsic viscosities of the blends are linear functions of blend composition to a good approximation. Huggins coefficients display nonlinear dependencies on blend composition. Both positive and negative deviations from perfect behaviour can be observed. These dependencies are governed by the difference in Huggins coefficients, $K_{12} - (K_1K_2)^{1/2}$, where the quantities characterise the blend and the geometric mean of the parent components, respectively. Positive deviations from perfect behaviour originate from attractions between the polymer species that enhance swelling of the coils. This behaviour was observed for blends of PHB and PEO. It was not influenced by molecular mass. Opposite deviations could be detected for blends of PHB and PCL indicating repulsions between the coils that lead to immiscibility.

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