

Miscibility Behavior of Polyacrylamides Poly(Ethylene Glycol) Blends: Flory Huggins Interaction Parameter Determined by Thermal Analysis

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ABSTRACT

Blends of polyacrylamide—PAM, poly(N-isopropylacrylamide)—PNIPAAm, poly(N-tert-butylacrylamide)—PTBAA, poly(N,N-dimethylacrylamide)—PDMAA and poly(N,N-diethylacrylamide)—PDEEA with poly(ethylene glycol)—PEG were prepared by casting in methanol and water at concentrations of 20 wt%, 40 wt%, 60 wt%, and 80 wt% in PEG. The miscibility of the components was studied by Differential Scanning Calorimetry—DSC. All blend systems are characterized by a single glass transition temperature (T_g), close to the T_g of the amorphous component. The Hoffman Weeks method was used to determine equilibrium melting temperature (T_m) data. The determination of the melt point depression of the blends allowed the calculation of Flory-Huggins interaction parameter (χ_{12}) of the two polymers in the melt, by using the Nishi Wang equation. The interaction parameters, calculated for all the blends, are slightly negative and close to zero, suggesting a partial miscibility between the components.

Keywords: Polyacrylamides; Poly(Ethylene Glycol); Polymer Blends; Flory-Huggins Interaction Parameter; Differential Scanning Calorimetry

1. Introduction

Most of the proposed applications of polyacrylamides rely primarily on their behavior in aqueous solution [1-4]. On the other hand, this polymer and some of its N-alkyl substituted derivatives show great potential in the preparation of miscible polymer blends due to their ability to interact through hydrogen bonding. Polyacrylamide—PAM, and some of its N-alkyl substituted derivatives, such as poly(N-isopropylacrylamide)—PNIPAAm, poly(N-tert-butylacrylamide)—PTBAA, poly(N,N-dimethylacrylamide)—PDMAA, and poly(N,N-diethylacrylamide)—PDEEA, are amorphous and water-soluble polymers with great industrial and agricultural interest [5-7]. In previous work, Silva *et al.* [8] showed that their thermal behavior is strongly dependent on the alkyl bonded to the amide group. Polyacrylamides form gels, or polymer networks that are able to expand in compatible solvent, like water, exhibiting a great potential for concentration of macromolecules from solutions, water purification, enzyme immobilization, drug delivery, sensors and

for several biomedical uses [1,9-13].

Poly(ethyleneglycol), PEG, is a semi-crystalline polymer that shows applications as chromatographic support and polymeric electrolyte [14-18]. In the last ten years, interest has been attracted to systems in which at least one of the components is crystallizable. In this case, a melt point depression of the crystalline phase relative to its melting point (T_m) in a non-interacting medium provides additional evidence of miscibility, since the kinetics and morphological effects over T_m are eliminated [19]. Measurement of the melting temperature (T_m) depression for blends allowed the determination of the Flory-Huggins interaction parameter (χ_{12}) of polymers in the melt state, by using the Nishi-Wang equation [20,21]. The Hoffman-Weeks method is used to determine the equilibrium data [22].

There have been many studies on miscible blends containing poly(ethylene glycol) and poly(ethylene oxide). For example, blends of PEO/poly(epichlorohydrin) and PEO/poly(epichlorohydrin-co-ethylene oxide) were studied by Silva *et al.* [19]. For these systems, the polymer-polymer interaction parameters are all negatives and ex-

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hibit dependence on the blend composition, decreasing for blends rich in PEO, suggesting that the polymer pairs are thermodynamically miscible.

Cortazar *et al.* [23] and Cimmino *et al.* [24] studied blends of PEO/poly(methyl methacrylate) with several molecular weights, finding χ_{12} values in the range of -0.131 to -0.290 . Blends of PEO ($M_w = 2.0 \times 10^3$) and poly(*p*-hydroxybenzoic acid)—PHB, ($M_w = 2.79 \times 10^3$) are miscible and exhibit χ_{12} values of -0.21 to -2.00 , depending on the concentration of the crystalline component [25].

The miscibility of PVC/PEO blends was studied using viscosimetry, thermal analysis and microscopy by Neuro *et al.* [26]. χ_{12} values obtained from the melting point depression are dependent on the molar mass of PVC, varying from -0.102 to -0.028 , indicating that the pair is miscible in the melt.

In this paper, we report the study on the miscibility of blends of PAM, PNIPAAm, PTBAA, PDEAA e PDMAA with PEG, using differential scanning calorimetry (DSC). The Flory-Huggins interaction parameters (χ_{12}) were determined by the melting point depression method.

2. Experimental

2.1. Materials

PAM, PNIPAAm, PTBAA, PDMAA and PDEAA were synthesized via free radical mechanism, under nitrogen atmosphere, according to the method described by Freitas and Cussler [1].

Monomers (Aldrich and Polyscience) and the initiators, ammonium persulfate, sodium metabisulfite (Reagen), and 2,2'-azobisisobutyronitrile (Polyscience), analytical grade, were used as received.

PEG (Aldrich), $2000 \text{ g}\cdot\text{mol}^{-1}$, was used as received, without additional purification.

The weight-average molecular weight (M_w) of amorphous homopolymers was determined by light scattering using a Brookhaven Instruments equipment.

2.2. Blends Preparation

Binary blends of varying compositions were prepared by casting from water and methanol solutions. To ensure complete removal of the solvent, the blends were kept under vacuum at 41°C for ten days.

2.3. Blends Characterization and Determination of Crystallization Temperatures by DSC

The DSC curves for homopolymers and blends were obtained on a DSC-50 Shimadzu module. Samples weights were maintained in the range of 10 mg. All experiments were performed under helium flow of $70 \text{ mL}\cdot\text{min}^{-1}$. The samples were heated from ambient to 210°C at a rate of

$20^\circ\text{C}\cdot\text{min}^{-1}$, held at this temperature for 10 min to eliminate thermal history. After cooling the samples to -20°C at a rate of $20^\circ\text{C}\cdot\text{min}^{-1}$, they were heated again to 210°C at $10^\circ\text{C}\cdot\text{min}^{-1}$.

The glass transition temperature and the melting enthalpies (ΔH_m) values were taken from the second heating scan. The cooling scan was used to select the crystallization temperatures.

2.4. Isothermal Crystallization

Isothermal crystallization was performed on a DSC-50 Shimadzu module based on the Hoffman-Weeks method [22]. Samples weights of 10 mg were heated from 25°C to 200°C at a rate of $20^\circ\text{C}\cdot\text{min}^{-1}$, held at this temperature for 5 min, rapidly cooled (cooling rate $\sim 40^\circ\text{C}\cdot\text{min}^{-1}$) to the desired crystallization temperature (T_c), maintained at this temperature for 2 min, and then cooled to 10°C at a rate of $20^\circ\text{C}\cdot\text{min}^{-1}$. After that, the samples were heated to 200°C , at a rate of $20^\circ\text{C}\cdot\text{min}^{-1}$, for the measurement of the T_m . This procedure was repeated for different crystallization temperatures.

2.5. Scanning Electron Microscopy (SEM)

SEM micrographs of the blends were obtained using a JEOL JSM-5410 microscope and the samples were fractured in nitrogen and covered by sputtering with a Au/Pd alloy.

2.6. Density Measurements

Density measurements of each homopolymer were carried out using a picnometer in a non-solvent (heptane and cyclohexane).

3. Results and Discussion

The weight-average molecular weight of PAM and its *N-alkyl* substituted derivatives are, as seen in **Table 1**, at the same order of magnitude.

Density values of PAM and its *N-alkyl* substituted derivatives are showed in **Table 2**.

It's shown in **Figure 1** DSC curves of blends with 20

Table 1. Weight-average molecular weight of PAM and its *N-alkyl* substituted derivatives

Homopolymer	PAM	PNIPA Am	PTBAA	PDMAA	PDEAA
$M_w \times 10^{-5}/\text{g}\cdot\text{mol}^{-1}$	2.53	1.20	2.07	2.74	1.15

Table 2. Density values of homopolymers.

Polymer	PAM	PNIPAAm	PTBAA	PDMAA	PDEAA	PEG
Density/ $\text{g}\cdot\text{mL}^{-1}$	1.05	0.97	0.89	0.89	0.89	1.31

wt%, 40 wt%, 60 wt% and 80 wt% PEG. T_g values are listed in **Table 3**. A single T_g is observed for all blends and it does not change appreciably with the composition, showing values around T_g of the amorphous polymer (PAM and its *N-alkyl* substituted derivatives), suggesting that the amorphous phase of the blend is rich in this component. The blends also show a single endothermic peak due to the melting of crystalline phase (PEG).

Figure 2 shows scanning electron micrographs of PAM, PEG and PAM/PEG blends in various compositions. It is observed that the crystal sizes are dependent on the amorphous polymer concentration. As the amorphous polymer concentration increases, PEG crystalline phase size decreases (**Table 4**). It is known that the kinetics of crystallization of the crystalline component in a blend is affected by the presence of the amorphous polymer [27,28]. Both, the overall kinetic rate and the spherulites growth rate decrease significantly. Changes on crystallization behavior are due to low mobility of PEG related with T_g of the blends and with the possibility of favorable interactions between PEG and the amorphous polymer.

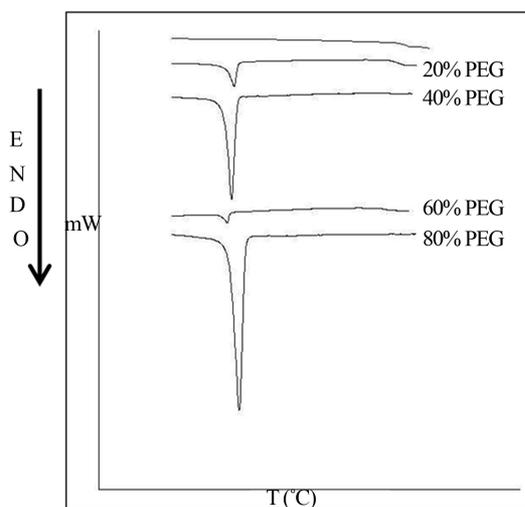


Figure 1. DSC curves for PAM/PEG.

Table 3. T_g values of PAM/PEG and their blends.

PEG/ %.ww ⁻¹	PMA/ PEG	PNIPAAm/ PEG	PTBAA/ PEG	PDMAA/ PEG	PDEAA/ PEG
0	188	142	128	111	91
20	178	133	84	98	88
40	174	126	84	90	85
60	166	126	87	83	83
80	163	126	83	79	83
100	-52*	-52*	-52*	-52*	-52*

*Silva et al. [8].

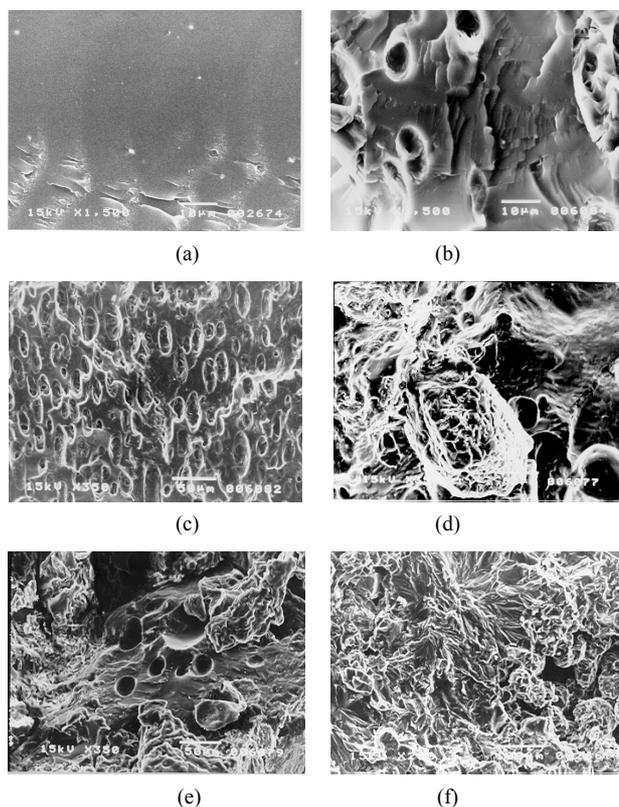


Figure 2. SEM micrographs; (a) pure PAM; (b) 20% PEG; (c) 40% PEG; (d) 60% PEG; (e) 80% PEG; (f) pure PEG.

Table 4. PEG crystals average diameters (d_m) of PAM/PEG blends.

PAM/% m-m ⁻¹	20	40	60	80
$d_m/\mu\text{m}$	24	24	20	14

Determination of Flory-Huggins Parameter

In blends in which at least one component is crystallizable, the melt point depression of the crystalline phase relative to its melting point provides additional evidence of miscibility. The melting point of a polymer is affected not only by the thermodynamic factors but also by the morphological aspects such as crystalline lamellar thickness. As described by the Flory-Huggins theory, the equilibrium melting point should be used to separate morphological effect from thermodynamic effect in discussing the melt point depression [29].

Morphological effects are associated with changes in crystal perfection or geometry and with different thermal history of the samples. The contribution of such morphological effects can usually be removed by constructing a Hoffman-Weeks [22] plot by using melting data for PEG and for blends isothermally crystallized at different temperatures (T_c); T_{me} is determined by the extrapolation of the experimental curve of T_m versus T_c to theo-

retical curve, $T_m = T_c$.

Thermodynamic considerations predict that chemical potential of a crystallizable polymer will decrease caused by the addition of the miscible diluent [28]. The expression to describe the dependence of the melting point depression due only to thermodynamic effects on the blends composition is given, according to the Flory-Huggins theory modified by Nishi-Wang, by Equation (1) [20,21].

$$\frac{1}{T_{me}} - \frac{1}{T_{me}^0} = -\frac{RV_{2u}}{\Delta H_{2u}V_{1u}} \left[\frac{\ln \phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1} \right) \phi_1 + \chi_{12} \phi_1^2 \right] \quad (1)$$

T_{me} e T_{me}^0 are the equilibrium melting temperature of PEG in blends and pure PEG, respectively. Subscripts 1 e 2 are referred to the crystallizable and non-crystallizable polymers, V_u is the molar volume of the repeating unit, ΔH_u is the heat of fusion of the perfectly crystallizable polymer per mole of the repeat unit, m is the degree of polymerization; ϕ are the volume fractions, R is the universal gas constant, and χ_{12} is the polymer-polymer interaction parameter.

Figure 3 shows the Hoffman-Weeks plots for isothermally crystallized blends.

Table 5 summarizes the equilibrium melting temperatures of PEG in the blends (T_{me}). For pure PEG, equilibrium melting point (T_{me}^0) was determined as 57°C. In

general, T_{me} values showed a slight decreasing tendency relative to T_{me}^0 value as the concentration of the amorphous component increases.

Table 6 shows ϕ_1 and ϕ_2 values used to calculate χ_{12} . R and ΔH values were 8.31 J·K⁻¹·mol⁻¹ and 7.90 K·J·mol⁻¹, respectively.

In **Figure 4** and in **Table 7**, χ_{12} values are represented as a function of PEG composition.

For all systems, χ_{12} values are dependent on the blend composition. Avella [25] and Yoo [30] attribute the dependence of χ_{12} on the blend composition to morphological and kinetics factors such as recrystallization, phase segregation, etc. Painter *et al.* [31] proposed that this effect results from the strong interactions between the components as hydrogen bonding observed in poly(vinyl

Table 5. Equilibrium melting temperatures of PEG in the blends.

$T_{me}/^{\circ}\text{C}$					
PEG/ % m·m ⁻¹	PAM/ PEG	PIPAA/ PEG	PTBAA/ PEG	PDMAA/ PEG	PDEAA/ PEG
20	54	52	53	56	52
40	56	56	55	53	55
60	56	56	56	55	56
80	56	56	56	56	56

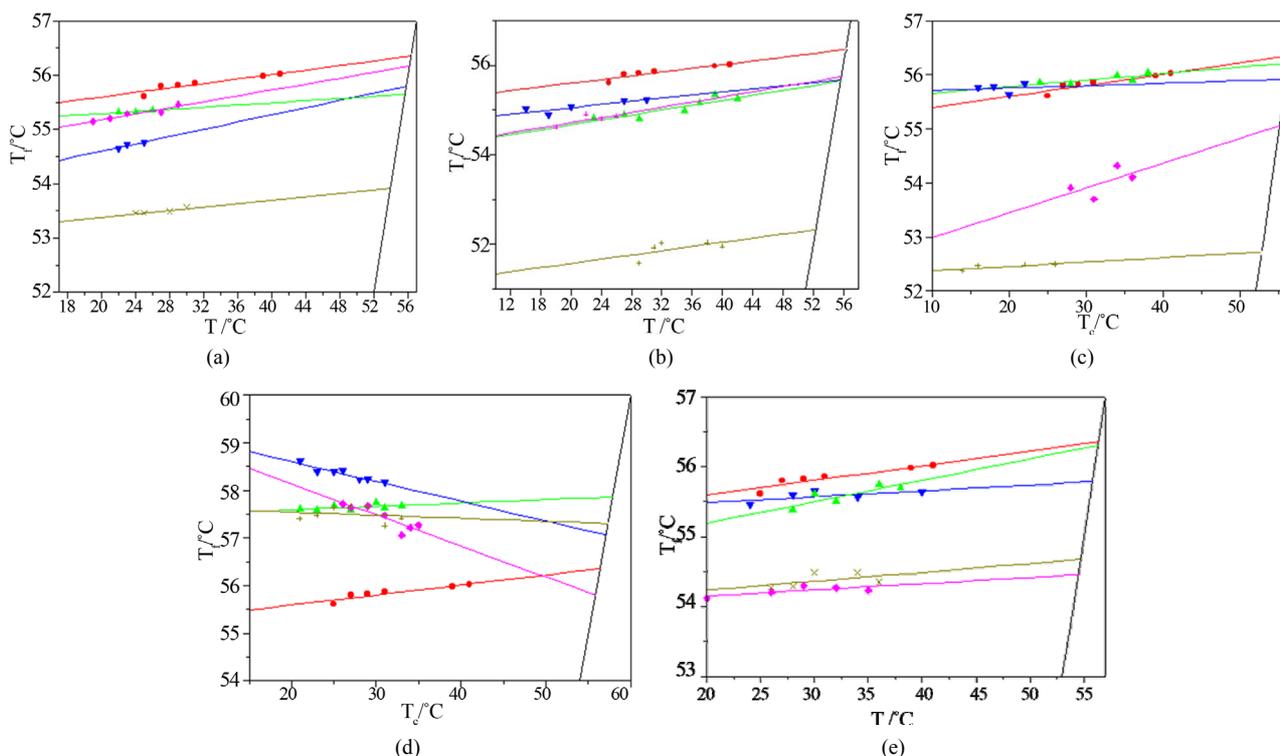
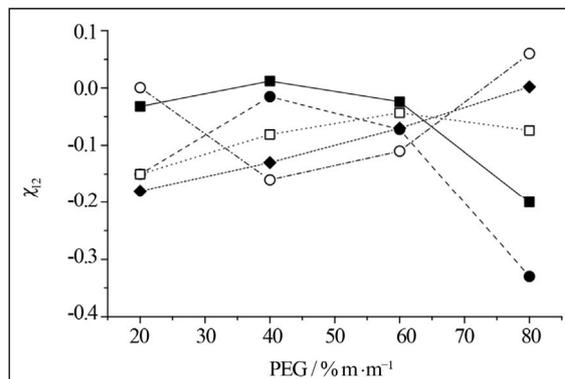


Figure 3. Hoffman-Weeks plots of isothermally crystallized blends. PEG (wt%): (●) 100; (---) 80; (■) 60; (◆) 40 e (+) 20% m·m⁻¹; (a) PAM/PEG; (b) PNIPAAm/PEG; (c) PTBAA/PEG; (d) PDMAA/PEG; (e) PDEAA/PEG.

Table 6. ϕ_1 and ϕ_2 values.

PEG/% m·m ⁻¹	PAM/PEG		PIPAA/PEG		PTBAA/PEG		PDMAA/PEG		PDEAA/PEG	
	ϕ_1	ϕ_2	ϕ_1	ϕ_2	ϕ_1	ϕ_2	ϕ_1	ϕ_2	ϕ_1	ϕ_2
20	0.84	0.16	0.85	0.15	0.85	0.15	0.85	0.15	0.86	0.14
40	0.66	0.34	0.67	0.33	0.69	0.31	0.69	0.31	0.70	0.30
60	0.47	0.53	0.48	0.53	0.49	0.51	0.49	0.51	0.51	0.49
80	0.25	0.75	0.25	0.75	0.27	0.73	0.27	0.73	0.28	0.72

**Figure 4.** χ_{12} versus blends composition: (■) PAM/PEG, (●) PNIPAAm/PEG, (□) PTBAA/PEG, (○) PDMAA/PEG e (◆) PDEAA/PEG.**Table 7.** χ_{12} values as a function of PEG concentration.

PEG/ % m·m ⁻¹	χ_{12}				
	PAM/ PEG	PIPAA/ PEG	PTBAA/ PEG	PDMAA/ PEG	PDEAA/ PEG
20	-0.032	-0.15	-0.15	7.2 × 10 ⁻⁴	-0.18
40	0.012	-0.015	-0.081	-0.16	-0.13
60	-0.024	-0.072	-0.043	-0.11	-0.070
80	-0.20	-0.33	-0.074	0.060	2.0 × 10 ⁻³

phenol) and poli(ethylene-co-acrylic acid) blends. Lee *et al.* [32] studying, by DSC, blends of polystyrene and polybutadiene, found χ_{12} values in the range of 0.0040 to 0.0102, depending on the blend composition and on the molar mass of the homopolymers. Linares and Acosta [33] studied PVDA/PVA and PVDF/PMMA blends and found χ_{12} values in the range of -0.164 to 2.025×10^{-3} and of -0.153 to 2.201×10^{-3} , respectively, indicating, according to the authors, that these systems are partially miscible.

Blends of poly(vinyl alcohol) and Nylon 6 were studied by Koulouri and Kallitsis [34], through dynamic-mechanical analysis (DMA), DSC and the Nishi-Wang equation to determine Flory-Huggins parameters. The results showed a single T_g and the χ_{12} value was -0.05 , suggesting miscibility. Others χ_{12} values and their analysis as

criterion of miscibility for blends can be found in Zhang *et al.* [28], Marcos *et al.* [35], and Cimmino *et al.* [24].

Miscibility was investigated in blends of poly(butylene succinate) (PBSU) and poly(vinyl phenol) (PVPh) by Qiu *et al.* [36]. The existence of single composition dependent glass transition temperature and the negative values of χ_{12} , calculated using the Nishi-Wang equation, indicate that PBSU/PVPh blends are thermodynamically miscible in the melt.

Oréface *et al.* [29] determined the degree of interaction between the components of a polycarbonate-polystyrene blend through the Flory-Huggins interaction parameter. The results showed that blends with higher content of polycarbonate tend to present χ_{12} closer to the critical values, suggesting greater compatibility in these compositions.

High molecular weight samples of the novel biodegradable polyester poly(ethylene sebacate) (PESeb) with poly(4-vinyl phenol) (PVPh) blends were studied, with respect to miscibility, by Papageorgiou *et al.* [37]. A single glass transition temperature intermediate to those of pure components was observed in all blends. Melting point depression was observed with increasing content of the amorphous polymer. The equilibrium melting points were estimated using Hoffmann-Weeks extrapolation. The interaction parameter was calculated and it was found to be $\chi_{12} = -1.3$. Blends miscibility was attributed to the formation of hydrogen bonds between the hydroxyl groups of PVPh and carbonyl groups of PESeb.

In the present work, χ_{12} values are dependent on the blend composition and are near zero or slightly negatives (Table 7), suggesting partial miscibility between PEG and the amorphous polymers in the melting, maybe as a result of interactions through hydrogen bonds. Additionally, T_g behavior and SEM micrographs corroborate this result.

4. Conclusion

Binary blends of polyacrylamide and some of its *N*-alkyl substituted derivatives with PEG, obtained by co-dissolution method, are partially miscible, as demonstrated by the smooth lowering of T_g values relative to the T_g value of the pure amorphous component. The polymer-polymer

interaction parameters obtained from thermodynamic melting temperature depression analysis are slightly negative and close to zero, suggesting partial miscibility among the components. Furthermore, for all blends studied, there is an endothermic peak corresponding to the melting of the PEG crystalline phase. For all blends studied, SEM micrographs indicate the presence of PEG crystalline phase.

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