ELSEVIER

Polymer 44 (2003) 1075–1080

polymer

www.elsevier.com/locate/polymer

Thermodynamics of pseudo-ternary systems as a tool to predict the morphologies of cellulose acetate/polystyrene blends cast from tetrahydrofuran solutions

Gislaine A. Silva[a], John Eckelt[b], Maria C. Gonçalves[a,*], Bernhard A. Wolf[b]

[a]Institute of Chemistry, Universidade Estadual de Campinas, 13083-970 Campinas, SP Brazil
[b]Institut für Physikalische Chemie der Johannes Gutenberg, Universität Mainz, Mainz, Germany

Received 17 July 2002; received in revised form 8 November 2002; accepted 14 November 2002

Abstract

The demixing behavior of the ternary system THF/CA/PS (tetrahydrofuran/cellulose acetate/polystyrene) was investigated at 25 °C. Cloud point measurements show that the system exhibits a large miscibility gap caused by the incompatibility of CA and PS. Both ends of the experimentally determined tie lines are located inside the two-phase area of the phase diagram. By means of the measured critical composition of the ternary system and the Flory–Huggins interaction parameters published for two of the binary subsystems ($\chi_{\mathrm{CA/THF}} = 0.442$ and $\chi_{\mathrm{PS/THF}} = 0.475$) the polymer/polymer interaction parameter was adjusted (directly minimizing the Gibbs energy) to $\chi_{\mathrm{CA/PS}} = 0.057$. These thermodynamic data were used to calculate the extension of the metastable and the unstable regions of the phase diagram. This procedure permits a realistic prediction of the morphologies of the (solvent-free) blends from the location of the starting composition of the casting solutions in the Gibbs phase triangle, as demonstrated by means of optical micrographs and field emission scanning electron micrographs.

Keywords: Cellulose acetate; Ternary system; Morphology

---

1. Introduction

Cellulose acetate (CA) is a polymer produced primarily from cellulose. It has great industrial importance, the applications of which include fibers, films and injection-molded thermoplastics, the last being commercially attractive [1,2]. It is a tough material with an excellent optical clarity. These advantageous properties are balanced out by limitations especially in its mechanical performance. Preparation of blends is one potential route for overcoming these disadvantages. However, blends of CA and commercial synthetic polymers, such as polystyrene (PS), exhibit a two-phase morphology, where the size of the domains strongly influences the final properties as well as the interface adhesion between the dispersed phase and the matrix. The different possible structures depend on the composition of the mixture and on the thermodynamic interaction between CA and PS. Information on the location and extension of the unstable region (typical for the co-continuous morphologies resulting from spinodal decomposition) and on the area of metastability (typical for dispersed structures obtained via nucleation and growth) is therefore a powerful key to control the final properties of the blends. For the above reason, it was one of the objectives of this work to determine the binary interaction parameters between the polymers from the phase behavior of their solutions in the common solvent tetrahydrofuran (THF). In this manner one can tailor the conditions required for the attainment of desired morphologies.

1.1. Theoretical background

The Gibbs energy of mixing per mole of segments, $\Delta\overline{\overline{G}}$, for polymer containing systems with K components is often

---

* Corresponding author. Tel.: +55-19-3788-3129; fax: +55-19-3788-3023.
E-mail address: maria@iqm.unicamp.br (M.C. Gonçalves).

0032-3861/03/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0032-3861(02)00869-8

described by the Flory–Huggins equation [3,4]

$$\frac{\Delta \overline{\overline{G}}}{RT} = \sum_{i=1}^{K} \frac{1}{N_i} \varphi_i \ln \varphi_i + \sum_{i=1}^{K-1} \sum_{j=i+1}^{K} g_{ij}\varphi_i\varphi_j \qquad (1)$$

where N_i is the number of segments of a molecule of component i in a mixture of K components, φ_i the fraction of segments of a certain component in the system and g_{ij} corresponding to the binary (integral) interaction parameters between the components i and j.

For a binary system and setting the molar volume of the solvent equal to the volume of a segment equation (1) reduces to

$$\frac{\Delta \overline{\overline{G}}}{RT} = \varphi_1 \ln \varphi_1 + \frac{\varphi_2}{N_2} \ln \varphi_2 + g\varphi_1\varphi_2 \qquad (2)$$

The interaction parameter is related to the chemical potential of the solvent μ_1, i.e., the Gibbs energy of dilution $\Delta\overline{\overline{G_1}}$, by

$$\frac{\Delta \overline{\overline{G_1}}}{RT} = \frac{\Delta\mu_1}{RT} = \ln(1-\varphi_2) + \left(1 - \frac{1}{N_2}\right)\varphi_2 + \chi\varphi_2^2 \qquad (3)$$

where χ represents the Flory–Huggins parameter (as obtained from the Gibbs energy of dilution, i.e., from the chemical potential of the solvent).

Information on χ from measured phase diagrams is usually obtained from the condition that the chemical potential of the component under consideration (cf. the above relation) be equal in the coexisting phases. For ternary systems, such calculations are often rather laborious. For that reason a new fitting method [5–7] uses the requirement that the free energy of the entire system must assume its minimum value under equilibrium conditions. The observed liquid–liquid phase separation behavior (cloud points and tie lines) of the ternary system was therefore evaluated with this procedure [6] not requiring chemical potentials. It gives access to binodals, spinodals, tie lines and critical points.

2. Experimental

2.1. Materials

The solvent THF (content > 99.5%, density = 0.889 g/cm^3 at 25 °C) was purchased from Fluka (Buchs, Switzerland) and used without further treatment. CA (30*n*), with a number average molecular mass of 30 kg/mol, an average degree of substitution of 2.5, and a density of 1.30 g/cm^3 at 25 °C, was supplied by Aldrich. PS (250*n*) was supplied by Proquigel and has a number-average molar mass of 250 kg/mol and a density at 25 °C of 1.03 g/cm^3. Both polymers have broad molecular weight distributions. The polydispersity index M_w/M_n is 2.35 for CA and 2.73 for PS. These data were determined using a GPC Waters 486 system, Ultrastyragel 7.8 per 300 mm, 500, 10^3 and 10^4 in series where THF was the solvent. PS was used for calibration; this means that the molar masses of CA are apparent values only.

2.2. Cloud points

The cloud points were determined visually at 25 °C by titrating 10.0 g of homogeneous solutions of CA in THF with homogeneous solutions of PS in THF or vice versa. The polymer content of the solutions varied between 4 and 6% (w/w). The composition of the mixtures was determined by weighing.

2.3. Critical point

After reaching the cloud point of the ternary mixture, e.g., when the system became cloudy, as for the turbidimetric titration, then two further drops of the standard solution (CA in THF or PS in THF) were added to guarantee macroscopic phase separation; in this manner, the overall composition of the system is kept almost identical to that of the cloud point. This system was then heated to 40 °C for homogenization and thereafter slowly cooled to 25 °C, where two macroscopically separated phases form upon standing. The volumes of these coexisting phases were determined and their ratio was plotted versus the concentration of CA or PS. The critical weight fractions w_{CA} or w_{PS} can be determined [8] from the condition that this ratio approaches unity at the critical point.

2.4. Tie lines

For the determination of the compositions of coexistent phases, different mixtures within the two-phase area of the phase diagram were prepared. These mixtures were kept in tightly sealed tubes, stirred overnight at 40 °C and then cooled to 25 °C. The system was kept at 25 °C to allow the formation of two macroscopic phases. After their separation, the solvent from the phases was removed in a vacuum line and the reminder was weighed to give the amount of the polymer. The weight fraction of the polymers in the residual blend was determined from the peak areas obtained in GPC experiments.

2.5. Morphology

In order to evaluate the morphology for the binary system CA/PS, some films were prepared from solution casting. Three droplets of the THF/CA/PS mixture were placed on a microscopic glass slide and the solvent was allowed to evaporate during 1 h at room temperature. The morphology formed from the dry thin film was evaluated by optical microscopy using a Zeiss optical microscope Photo-Mikroskop III. The morphology of thick films was also studied. Fracture surfaces were obtained by bending film pieces under liquid nitrogen; these were carbon- and gold-coated in a Bal-Tec MD 020 instrument and examined in a JEOL JSM-6340F field emission scanning electron microscope, operated at 3 kV.

3. Results and discussion

3.1. Phase diagram

The phase diagram for the THF/CA/PS ternary system obtained at 25 °C is depicted in Fig. 1. As mentioned before, CA and PS are incompatible showing two-phase separation behavior.

The Gibbs phase triangle, which describes the limit of stability and composition of separated phases at equilibrium, can be obtained experimentally for a particular system. This involves measuring the cloud point curve that represents the border between compositions that are completely stable in a single phase and those that are unstable or only metastable. This is an experimental curve that closely matches the binodal curve in most practical situations. Deviations occur because polymer solutions are rarely monodisperse and some fractionation in the molecular weight will take place.

Fig. 1 shows the cloud point curve, the tie lines and the critical composition, as obtained from the measured phase volume ratios evaluated in Fig. 2. The values resulting for the critical weight fractions of the CA and PS are 0.025 and 0.017, respectively.

The compositions of the coexistent phases were determined at 25 °C (Table 1). As can be seen in Fig. 1, an important feature lies in the fact that both end points of the tie lines (dotted lines) are located inside the cloud point curve. A displacement from this line, such that one end lies inside and the other outside, is normal and results from the polydispersity of the polymer samples, which is rather high in the present case (CA = 2.35; PS = 2.73). This behavior is due to the fact that the molecular weight distribution of the material contained in the equilibrium phases is different and no longer identical to that of the original sample, which was used in the cloud point measurements. An example for the uncommon behavior of the present system has already been reported in literature [9] for the ternary system chloroform/poly-L-(lactic acid)/poly(methyl methacrylate). According to model calculations based on continuous thermodynamics, this peculiarity is bound to large molecular non-uniformities of both blend components [9].

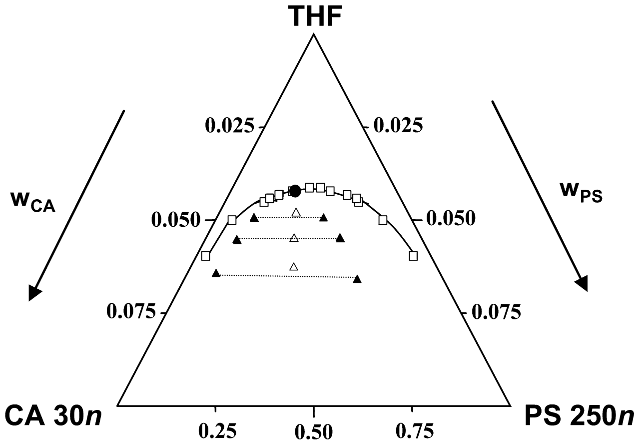


Fig. 1. Phase diagram of the THF/CA/PS ternary system close to the solvent corner at 25 °C. Experimental data: cloud point (open square); critical point (full circle) and tie lines (dotted lines).

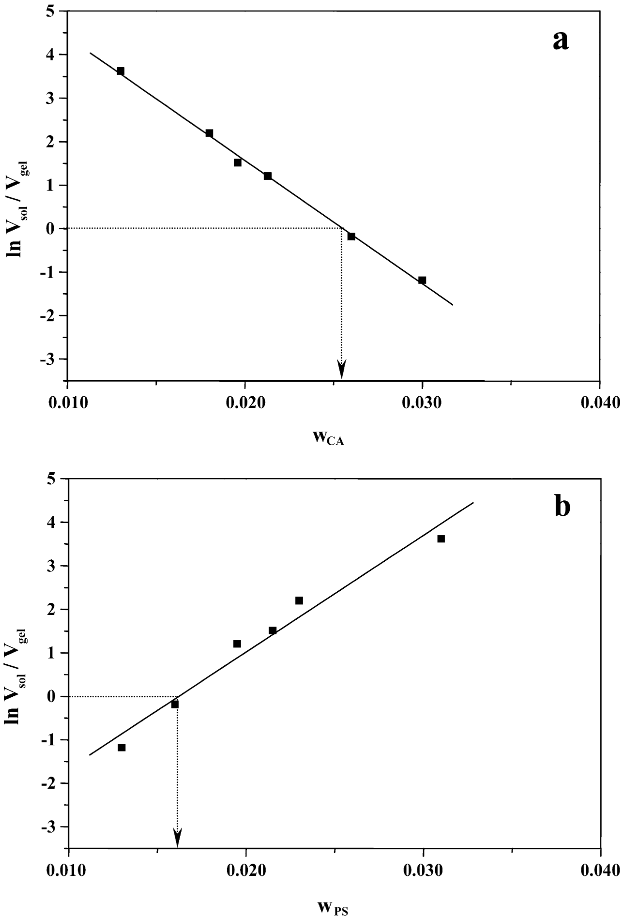


Fig. 2. Phase volume ratio of sol and gel phase as a function of the weight fraction: (a) CA; (b) PS. The critical content of CA and PS is indicated by dotted lines.

On the basis of the experimental data for the present system, interaction parameters can be determined by fitting calculated phase diagrams to the experimental data. For the

Table 1
Tie lines for the ternary system THF/CA/PS measured at $T = 25$ °C

Tie line	Original solution		PS-rich phase		CA-rich phase	
	w_{CA}	w_{PS}	w_{CA}	w_{PS}	w_{CA}	w_{PS}
1	0.028	0.019	0.020	0.029	0.039	0.011
2	0.032	0.022	0.020	0.035	0.047	0.008
3	0.035	0.025	0.021	0.045	0.058	0.007

Table 2
Parameters used for modeling of the phase diagram at $T = 25$ °C

	$T = 25$ °C
ρ_{CA} (g/cm^3)	1.30
ρ_{PS} (g/cm^3)	1.03
ρ_{THF} (g/cm^3)	0.88
M_{CA} (kg/mol^1)	30.00
M_{PS} (kg/mol^1)	250.00
M_{THF} (kg/mol^1)	0.07211
$N_{\text{segments of CA}}$	281
$V_{\text{segments of PS}}$ (cm^3/mol^1)	2952.01
$V_{\text{segments of THF}}$ (cm^3/mol^1)	1.00
Interaction parameter χ concentration independent	
$\chi_{CA/THF}$	0.442[a]
$\chi_{PS/THF}$	0.475[b]
$\chi_{CA/PS}$	0.057

[a] See Ref. [10].
[b] See Ref. [11].

THF/CA and THF/PS binary subsystems, the interaction parameters have been reported in literature [10,11], on the other hand, parameters for the interaction between polymers are scarce and hard to obtain directly. For that reason we have treated $\chi_{CA/PS}$ as a fit parameter independent of the concentration of CA and PS and varied it until the calculated critical point was situated on the experimental cloud point curve. Table 2 lists the parameters of these calculations and Fig. 3 shows the phase diagram modeled for the THF/CA/PS ternary system.

The calculated phase diagram, though qualitatively correct, does not coincide with the experimental data. There are a number of reasons that can explain that finding. First of all the interaction parameter for THF/PS, taken for the calculation, stems from inverse gas chromatography and refers to about 200 °C. Furthermore, polydispersity was neglected as was the composition dependence of different interaction parameters. Despite these simplifications the result offers a valuable guide to estimate the extension of the metastable and the unstable areas required for the discussion of the morphologies observed with films prepared along different routes through the phase diagram.

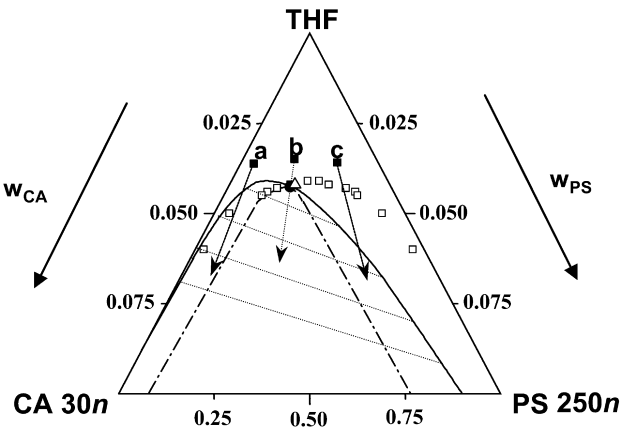
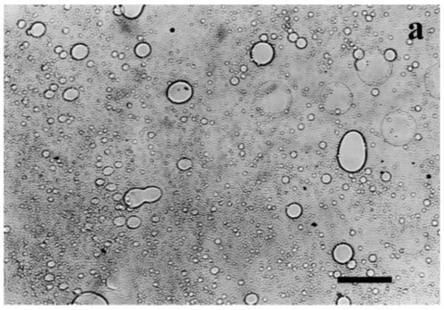
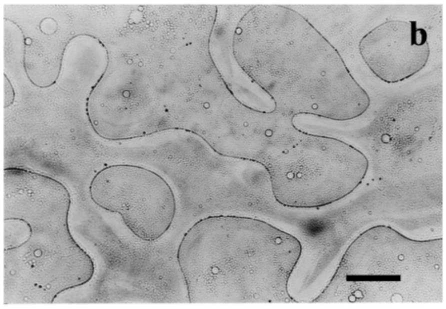


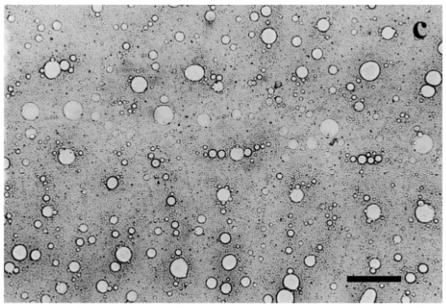
Fig. 3. Phase diagram of the THF/CA/PS ternary system at 25 °C. Theoretical data: binodal (thick line); spinodal (dash-dotted line); tie lines (dotted lines) and critical point (open triangle). Experimental data: cloud point (open square) and critical point (full circle). The dark squares (a, b and c) represent the starting compositions of different homogeneous solutions of CA and PS in THF, employed for film preparation.



Starting solution ***a***



Starting solution ***b***

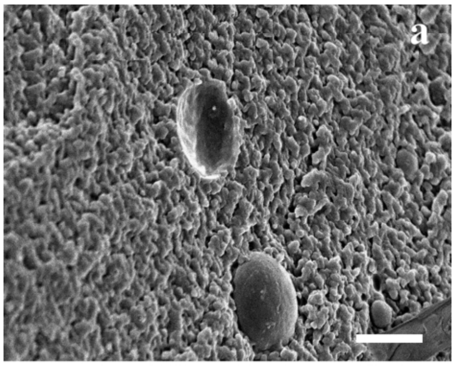


Starting solution ***c***

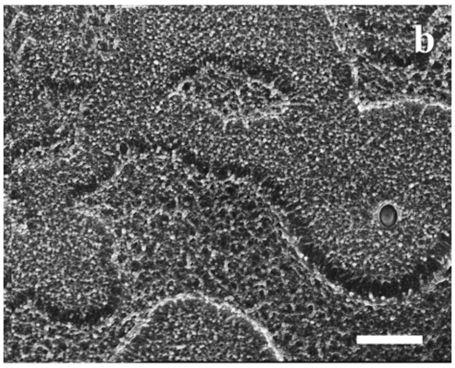
Fig. 4. Optical micrographs of films obtained from homogeneous solution of CA and PS in THF, as indicated in Fig. 3. Scale bars: 10 μm.

Table 3
Compositions of the casting solutions to evaluate the morphology

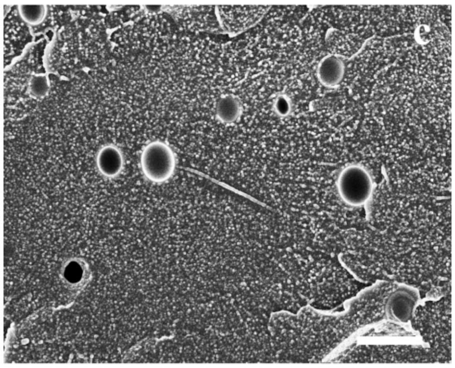
Solution	Weight fractions	
	w_{CA}	w_{PS}
a	0.035	0.005
b	0.023	0.015
c	0.015	0.023



Starting solution ***a***



Starting solution ***b***



Starting solution ***c***

Fig. 5. Field emission scanning electron micrographs of films obtained from homogeneous solution of CA and PS in THF, as indicated in Fig. 3. Scale bars: 10 μm.

3.2. Morphology of CA/PS blends

Immiscible polymers lead to heterogeneous systems. The resulted morphology depends on the nature of the polymers (interfacial tension, viscosities and the ratio of these viscosities), on their volume fractions and on the processing conditions. Furthermore, kinetic aspects (such as spinodal decomposition or nucleation and growth) play an important role. With respect to the influences of different pathways through the phase diagram in the course of solvent removal, we have performed some targeted experiments. Table 3 lists the different starting compositions of the casting solutions and Fig. 3 indicates the way through the metastable or unstable regions of the ternary phase diagram.

Starting from the composition indicated in Fig. 3 by the letter 'b', the mixture passes through the critical point (experimental and theoretical) and enters the unstable region practically without passing the metastable regime. This means phase separation through spinodal decomposition mechanism and the development of a co-continuous morphology occurs. In contrast to this situation, the solutions indicated in that graph with 'a' and 'c' must pass through the cloud point curve far from the critical point. In this case, the phase separation occurs at an extended metastable region and thus through the process of nucleation and growth. This morphology is characterized by dispersed domains of one phase in a matrix of the other. In point 'a', the CA-rich phase forms the matrix and conversely in point 'c' it is the PS-rich phase. Optical and scanning electron micrographs of the films obtained in the described manner are shown in Figs. 4 and 5.

The different micrographs shown in the last two figures confirm the theoretically postulated morphologies.

4. Conclusion

By means of the present investigation, it was demonstrated how experimental knowledge of the phase diagram of solutions of incompatible polymers in a common solvent, can be used to obtain information on the thermodynamic interaction between the two types of macromolecules and to estimate the extension of the metastable and unstable regions in a realistic manner. Based on that data, it is furthermore possible to forecast and thus control the morphologies of the (solvent-free) polymer blend by means of the starting composition location of the casting solutions in the Gibbs phase triangle.

Acknowledgements

We wish to thank Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) on the Brazilian side and Deutscher Akademischer Austauschdienst (DAAD) on the German side for the financial support of this work through the exchange program PROBRAL. MCG acknowledges the support of FAPESP and Pronex/Finep/MCT.

References

[1] Wart H, Mülhaupt R, Schätzle J. J Appl Polym Sci 1997;64:231.
[2] Samios E, Dart RK, Dawkins JV. Polymer 1997;38(12):3045.

[3] Flory PJ. Principles of polymer chemistry. New York: Cornell University Press; 1953.
[4] Huggins ML. J Polym Sci A 1967;2:1221.
[5] Horst R. Macromol Theory Simulat 1995;4:449.
[6] Horst R. Macromol Theory Simulat 1996;5:789.
[7] Horst R. Macromol Theory Simulat 1997;6:427.
[8] Krause C, Wolf BA. Macromolecules 1997;30:885.
[9] Eckelt J, Enders S, Gonçalves MC, Queiroz DP, Wolf BA. Fluid Phase Equilib 2000;171:219.
[10] Mark JE. Physical properties of polymers handbook. Woodbury, NY: American Institute of Physics; 1990. chapter 14.
[11] Shiomi T, Kuroki K, Kobayashi A, Nikaido H, Yokoyama M, Tezuka Y, Imai K. Polymer 1995;36(12):2443.