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Phase separation of polymer blends in solution: A case study

Gianluca A. Mannella *, Francesco Carfì Pavia, Vincenzo La Carrubba, Valerio Brucato

Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali (DICAM), University of Palermo, Viale delle Scienze, Ed. 8, 90128 Palermo, Italy

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ABSTRACT

The phase behavior and phase separation features of the quaternary system poly-L-lactide (PLLA)/poly-rac-lactide (PLA)/dioxane/water were investigated. Experiments were performed with fixed total polymer concentration of 6 wt%, by varying the PLLA/PLA weight ratio. Blend weight compositions examined were 100/0, 80/20, 50/50, 20/80 and 0/100, at fixed dioxane/water weight ratio (87/13). Cloud point measurements reported that the demixing temperatures of blends are close to PLLA in the same mixed solvent, in line with the calculated spinodals. As regards to foam preparation, above the PLA cloud point, morphology is similar to pure PLLA foams; conversely, below PLA cloud point, the morphology resulted highly inhomogeneous. This behavior could be related to a change in equilibrium conditions occurring close to PLA cloud point. The equilibrium measurements performed gave out results in line with this hypothesis.

1. Introduction

Phase separation phenomena in polymer solutions are widely used to produce porous structures. Along decades, many research groups have studied the thermodynamic and kinetic properties of polymer solutions [1–15], in order to achieve a better control in membranes and foams production processes. The most widely model system studied is a ternary solution composed by a polymer, a solvent and a nonsolvent, which has the function of promoting phase separation.

Thermodynamic investigations are aimed to define the miscibility gap, and possibly the compositions of equilibrium phases formed during demixing. Information about phase boundaries are useful to design experimental protocols, by choosing appropriate system composition and temperature in order to promote phase separation [14,16–21]. Moreover, the separation mechanism (i.e. nucleation and growth or spinodal decomposition) can be deducted from complete phase diagrams, usually obtained with modeling works [1–3,13,22–24].

Kinetic investigations involve the determination of relationships between time and morphology, i.e. the mechanisms and growth rate of separating domains. Mainly, two approaches can be followed, which can be coupled to obtain a complete picture of involved phenomena: experimental investigation, usually performed via optical techniques [10,25–28], and simulations, typically based on Cahn–Hilliard model [7,8,29,30].

As regards to applications involving polylactides, the polymer species focused in this work, a number of studies concerned the investigation of phase separation in solution with 1,4-dioxane (solvent) and water (nonsolvent), discussing the role of various processing parameters (as system composition, demixing temperature and time) on foams morphologies [18,31–34].

A further step in phase separation technology concerns the production of materials based on polymer blends, instead of a single component. Solution blending is a easy way to obtain a multicomponent product, with the aim to improve the

* Corresponding author.
E-mail address: gianluca.mannella@unipa.it (G.A. Mannella).

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properties offered by each singular material. For example, in the field of polymeric scaffolds for tissue engineering purposes, blends give the opportunity to tune the biodegradation rate [35]. Otherwise, in the field of membranes for gas and liquid separation, blends allow to tune hydrophobicity [36], protein adsorption [37], selectivity [38]. Nevertheless, few studies are focused on the characterization of phase separation behavior of polymer blends in solution [39–41], or the preparation of porous structures via phase separation from quaternary systems [36–38,42].

Within this framework, the case study presented in the following aims to partially bridge the gap concerning phase separation in quaternary systems, by providing experimental data and discussion about possible demixing mechanisms. The model system, composed by poly-L-lactide (PLLA), poly-rac-lactide (PLA), dioxane and water was investigated by means of cloud point detection via light transmittance measurements and by preparing porous foams. Cloud point measurement defines the boundary between homogeneous and demixed state, thus providing information about the miscibility gap. The analysis of porous foams allows one to infer the phase separation mechanisms involved, and the influence of processing conditions as temperature and time on the resulting morphology.

2. Experimental

2.1. Materials

The polymers examined in this study were PLLA RESOMER® L 209 S and PLA RESOMER® MD Type R 208, both purchased from Boehringer-Ingelheim. The first one is a stereoregular polylactide (semicrystalline), whereas the second one is a racemic polylactide (amorphous). The solvents employed were deionized water and 1–4 dioxane (Sigma–Aldrich, used without further purifications).

All solutions were prepared with a total polymer concentration fixed to 6 wt% and a dioxane/water weight ratio of 87/13. The PLLA/PLA weight ratios examined were 100/0, 80/20, 50/50, 20/80 and 0/100.

2.2. Cloud point measurement

Cloud point curves for the ternary and quaternary systems were measured through an experimental apparatus based on light transmission detection, already employed for characterizing ternary systems [21,43]. The sample temperature, monitored with a very small thermocouple, was tuned via Peltier cells, which allow an accurate control in both cooling and heating operations [44].

Measurements were performed with two different protocols: "quasi-equilibrium" and "dynamic" cloud point. Quasi-equilibrium measurements consist in cooling stepwise the solution by 0.5 °C, with a step time lasting 5 min. The cloud point was reached when a light transmission decrease by at least 1% of initial value was recorded. The dynamic measurements were performed by continuously cooling the solution at 1 °C/min. The measurements were repeated twice or more to ensure results reproducibility.

An example of cloud point detection with both protocols is reported in Fig. 1. The onset of phase separation, related to a light transmittance reduction of 1%, coincides between the two methods. Afterwards, as thermal histories are different, the turbidity variations are not superimposed.

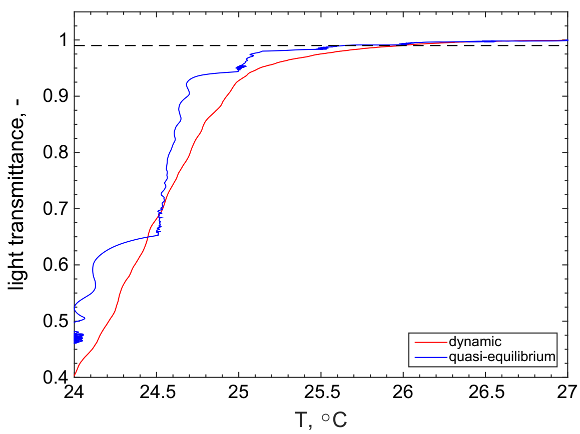

Fig. 1. Comparison between "quasi-equilibrium" and "dynamic" cloud point detection. The dashed line represent the threshold of 1% transmittance reduction.