



Water sorption thermodynamics in poly(propylene sebacate)



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ARTICLE INFO

Article history:

Received 4 April 2016

Received in revised form

16 May 2016

Accepted 18 May 2016

Available online 20 May 2016

Keywords:

Water sorption

Infrared spectroscopy

Hydrogen bonding

Poly(propylene sebacate)

NRHB

Biodegradable polyesters

ABSTRACT

Water sorption thermodynamics in poly-propylene sebacate, PPSeb, a biodegradable semi-crystalline polyester, has been studied above its glass transition temperature. Experimental results have been obtained by using gravimetric methods to determine water sorption isotherms at several temperatures, as well as by means of in-situ FTIR transmission spectroscopy, to obtain qualitative information and quantitative estimates on the self- and cross-Hydrogen Bonds occurring within the water-polymer mixture. In fact, the water-polymer system has been found to be populated by several water 'species', each one characterized by a particular configuration of HB interactions. Different moieties on the polymer backbone are involved in the formation of specific interactions.

The experimental results have been interpreted in the light of the Non Random Hydrogen Bonding (NRHB) lattice fluid theory for mixtures, which accounts both for the presence of Hydrogen Bonding (HB) interactions and for non randomness of the lattice contacts. An excellent fitting of experimental water sorption isotherms has been obtained, from which relevant mean-field and HB interactional parameters of the model have been calculated. On that basis, NRHB model has been then used to obtain qualitative and quantitative predictions, at equilibrium, of self and cross HB interactions involving both water molecules and groups present on the macromolecules within the polymer-water mixture, which compare well with the experimental results of FTIR spectroscopy.

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1. Introduction

Poly-propylene sebacate (PPSeb) is an aliphatic polyester that is semicrystalline at room temperature and displays a glass transition temperature and a melting temperature, as measured by differential scanning calorimetry, respectively equal to -53.1 °C and to 56.8 °C [1]. In view of its biocompatibility and fast biodegradability, PPSeb is of interest in the biomedical field, e.g. for the fabrication of porous scaffolds, for the production of eco-friendly foams and as shape memory polymer [1,2]. Quite interestingly, PPSeb can be considered as a bio-based polyester, obtainable from renewable resources, since raw materials for its synthesis can be extracted from industrially produced biomass. In fact, 1,3-propanediol (PDO)

can be produced via fermentation while the aliphatic dicarboxylic sebacic acid can be synthesized starting from castor oil.

The chemical structure of PPSeb suggests a relative hydrophobicity and a low water solubility, also confirmed by the experimental results reported in the present contribution, that make the behaviour of this biodegradable polymer similar, in this respect, to that displayed by semicrystalline Poly- ϵ Caprolactone (PCL). Both in PPSeb and in PCL water is sorbed within the amorphous phase which is, at room conditions, in an equilibrium rubbery state [3–7]. A detailed knowledge of water sorption thermodynamics in PPSeb, is required for proper use of this polymer to realize porous scaffolds or biomedical devices, since water solubility, along with water diffusivity, affects biodegradation kinetics in vivo. In this respect, a key role is played by the concentration of the possible different types of molecular aggregates involving water molecules which can form within the polymer-water phase. In fact, water molecules, due

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to their Hydrogen-Bonding (HB) capability, can either interact in different ways with the polymer matrix or can self-associate, also forming clusters, thus exhibiting different mobility within the system.

What described above motivates the interest in understanding, at a molecular level, the PPSeb-water mixture thermodynamics which is expected to display both self-HB interactions, occurring between water molecules, and cross-HB interactions occurring between water molecules and proton acceptor groups belonging to the polymer. To address these issues, one needs to rely upon proper experimental as well as theoretical approaches, able to deal with the underlined interactional aspects. To this aim, in this contribution, thermodynamics of water sorption in PPSeb is interpreted by using a theoretical approach that accounts for the occurrence of multiple specific interactions while experimental information on interactional issues is gathered by adopting an approach based on in-situ transmission FTIR spectroscopy. In fact, as demonstrated for several polymer-water systems, vibrational spectroscopy is well suited for obtaining qualitative and quantitative information on interactions occurring within the mixture. Here we use the results of the spectroscopic analysis to identify the groups involved in the specific interactions and to validate quantitative predictions of the thermodynamic model.

In view of the occurrence of several types of specific interactions involving water molecules absorbed within the amorphous polymer regions, one can identify different 'species' of water molecules. These 'species' range from water molecules that interact directly with specific groups along the polymer backbone (the so-called 'first shell water'), to water molecules interacting with 'first shell water' molecules (the so-called 'second shell water'), from water belonging to further shells located above the 'second shell water', to self-interacting water clusters and to non interacting water molecules dispersed within the polymer matrix. It is expected that the various 'species' of water molecules affect physical properties of a polymer-water mixture in a different way. Consequently, the overall water sorption uptake, obtained for instance from gravimetric measurements, taken alone does not provide the detailed physical picture that is needed for a thorough understanding of thermodynamics of polymer/water mixtures.

Molecular details on interactions occurring in polymer-water systems are made available by several spectroscopic techniques such as solid-state NMR, vibrational spectroscopy (IR, NIR, Raman), neutron scattering, light scattering [8,9]. Among these, it has been anticipated that FTIR has been proven to be the most powerful, very sensitive toward H-bonding detection and characterized by a significant sampling flexibility, which allowed us to implement sophisticated *in-situ*, *time-resolved* measurements [6,10]. In this respect, recent studies have afforded a deep molecular characterization of several polyester resins in terms of their sorption properties and H-bonding interactions with water. Different aggregates were identified and their concentration was estimated as a function of the overall amount of absorbed water. Details on the clustering mechanism were also obtained and discussed in terms of the systems' hydrophobic character [3–5].

In the literature, ad hoc models have been proposed for the analysis of sorption thermodynamics for the systems discussed above, addressing the case of rubbery amorphous polymers and explicitly accounting for the contribution of specific interactions. A relevant example, grounded on statistical thermodynamics and developed in the framework of compressible lattice fluids models, is the theoretical approach proposed by Panayiotou et al. [11–13], referred in the following as 'Non Random lattice fluid Hydrogen Bonding' (NRHB) model. In brief, modeling is based on the factorization of the configurational partition function for the polymer-penetrant system which is split in two different contributions.

The first one accounts for 'mean field' interactions while the other accounts for the presence of specific interactions. The 'mean field' contribution, in turn, consists in the combination of an 'ideal random' and in a 'non-random' contribution that has a form obtained on the basis of *Quasichemical* approximation [14]. This approach accounts for the non-randomness of all possible couples of 'mean field' interactions, including also those that involve the empty sites of the lattice (holes), whose presence allows compressibility to be accounted for in the lattice fluid scheme. The form of the term of the configurational partition function related to the presence of HB interactions is based on a combinatorial approach, first proposed by Veysman [15,16], that is integrated with the lattice fluid scheme.

A relevant advantage of NRHB theory is that it provides a relatively simple and efficient approach to cope with molecular association issues occurring in polymer mixtures endowed with complex hydrogen bonding behaviour. This approach has already been used in the literature [17] to describe sorption thermodynamics of several solvents, including water, in rubbery polymers in cases in which self-association of functional groups of the polymer as well as their cross-association with the low m. w. penetrant molecules do establish, obtaining in all cases a good quantitative interpretation of the experimental sorption isotherms. Mensitieri et. Al [3–7], have used the NRHB framework to model water sorption thermodynamics in Poly (ϵ -Caprolactone), PCL. The authors showed that the use of this model, originally developed for amorphous systems, can be successfully extended to the case of semicrystalline polymer-penetrant mixtures. To this aim, only a proper rescaling of the overall solubility with reference to the amorphous polymer content needs to be performed, assuming that the water sorption occurs only within the amorphous phase that displays the same thermodynamic behaviour that would occur in a totally amorphous polymer. Arguments supporting this approach are discussed in the paper by Bonavoglia et al. [18]. This simple biphasic framework has been adopted also in the present contribution. However, as will be discussed later, it is possible that the constrain effect exerted by crystalline domains, which is not accounted for by this simple approach, could actually play a role in impairing the predictive capability of NRHB model in terms of quantitative estimate of HBs established within the polymer-water system at hand.

In summary, the present contribution addresses the issue of sorption thermodynamics of water in PPSeb both experimentally, by combining gravimetric and FTIR spectroscopy analyses, and theoretically, by interpreting the results using the NRHB theory. In particular, are analysed here the HB self-interactions established among water molecules within the polymer-water mixture and in the water vapour phase, as well as the HB cross-interactions occurring between water molecules and the proton donor and acceptor groups present on the polymer backbone. In addition, are also investigated the different kinds of self-HB interactions that take place between several proton donor and proton acceptor groups of the polymer.

Qualitative information gathered from FTIR spectroscopy on HB interactions have been used to tailor the structure of the HB contribution in the NRHB model. In fact, only the most prominent interactions occurring in the system have been accounted for in writing the model equations. Once the structure of the model has been built, water sorption isotherms have been fitted by NRHB model equations. Then, the thermodynamic model has been used to perform a quantitative prediction of the amount of relevant HB interactions that have been compared with data provided by FTIR spectroscopy.

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