

Thermodynamics of water sorption in poly(ϵ -caprolactone): A comparative analysis of lattice fluid models including hydrogen bond contributions

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ABSTRACT

Thermodynamics of water sorption in poly(ϵ -caprolactone) (PCL) has been interpreted by using three models based on compressible lattice fluid theories, addressing the issue of self- and cross-hydrogen bond interactions. The models, available in the literature, are of increasing complexity and consist of a compressible lattice fluid term which could account or not for non-randomness of contacts and, in the case of two of the models, of a hydrogen bonding contribution.

Models were analysed and compared in terms of fitting capability of the experimental sorption isotherms and, where appropriate, of predicted amount of self- and cross-hydrogen bonds which are established in the PCL–water mixture. Results confirm that, to obtain a satisfactory fitting of data, it is necessary to explicitly account for formation of hydrogen bonds.

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1. Introduction

Poly(ϵ -caprolactone) (PCL) is a synthetic thermoplastic semi-crystalline polymer which is interesting for its biodegradability and biocompatibility [1–3]. It displays a low glass transition temperature (in the range from about -60 to -10 °C) [4] and a melting temperature of around 60 °C. This polymer is relatively hydrophobic and, among biodegradable polymers, exhibits low water solubility [5,6] which results in a relatively good barrier to moisture. In view of its properties, it is an interesting polymer for use in biodegradable food packaging and to make scaffolds for tissue engineering. These applications motivate the interest in understanding water sorption thermodynamics in PCL, which is expected to be characterized by possible self-interactions between water molecules sorbed in PCL and between water molecules and proton acceptor groups present on the polymer backbone. Modelling of equilibrium sorption thermodynamics for such systems should hence explicitly account for specific hydrogen bonding (HB).

Many efforts have been carried out in order to model sorption thermodynamics of low molecular weight compounds in polymers above their glass transition temperature. Among them, equation of state (EoS) approaches based on statistical thermodynamics, referred to as semi-theoretical EoS [7], provide an effective frame-

work to model thermodynamic properties and phase equilibria of mixtures of polymers and low molecular weight compounds. Two of the main classes of semi-theoretical EoS models proposed are those grounded on compressible lattice fluid theory (LF-EoS) [8,9] and those based on perturbation theory [10]. These theories have been widely employed to successfully predict solubility of gases and vapours in rubbery polymer systems in the cases in which specific interactions can be safely neglected. Among LF-EoS, are worthy of mention the random mixing compressible LF theory of Sanchez and Lacombe (SL) [11–13] and the random mixing hole theory of Simha and Somcinsky (SS) [14]. Conversely, on the basis of Wertheim's perturbation approach, several versions of Statistical Associating Fluid Theory (SAFT) have been proposed, developed in terms of residual Helmholtz energy, which is factorized in different contributions: number and types of factorization terms can vary depending on the specific model [15–20].

These approaches are well suited for systems which do not display specific interactions since, in the case of LF-EoS, only a mean field contribution is considered when constructing the expression of Gibbs energy for the mixture or, in the case of SAFT, interaction among components are accounted for only by a dispersive term in the residual Helmholtz energy expression. SAFT approach, however, offers the advantage of being built in a way that naturally allows for the inclusion in the model of short range interactions (association) and long range electrostatic interactions. In fact, several extensions of the original SAFT theory have been proposed to account for these effects [7,15–20]. Also LF theories

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have been further developed to include the effect of possible self- and cross-interactions in polymer–penetrant systems. In particular, Panayiotou and Sanchez [21] have modified the original SL LF-EoS theory [11–13] to account for the formation of specific interactions, i.e. hydrogen bonding (HB), in polymer–penetrant mixtures. This model, referred to in the following as PS, assumes that the configurational partition function can be factorized in two separate contributions: one related to mean field interactions and one accounting for the effects of specific interactions. The first contribution can be expressed, in principle, by using any available mean field LF theory. In particular, the PS model adopts, for the mean field contribution, the simple random mixing SL model [11–13] while the effect of HB interactions is accounted for by using a combinatorial approach first proposed by Veytsmann [22,23]. The same authors proposed a LF theory where an alternative way to account for the HB contribution was introduced by invoking the formation of multimers of association complexes [24]. This latter model and the PS model (differing only for the procedure of calculation of HB contribution) have been compared by Panayiotou [25], concluding that the combinatorial approach for HB, used in PS model, is more flexible and better suited for extension to more complex systems such as three dimensional HB network structures.

It is worth noting that the mean field LF theories described above, both the original ones and those modified to account for specific interactions, are based on a simplified statistical framework, in which the arrangement of *r*-mers and holes is assumed to be at random. However, in the case of non-athermal contacts between different kind of *r*-mers and/or holes, such an assumption is likely to be incorrect [26]. Based on the pioneering work of Guggenheim [8], several theories have been developed to deal with non-randomness distribution of contacts in LF systems, first tackling the cases in which occurrence of specific interactions is not accounted for. The basic idea is that the partition function can be factorized into an ideal random contribution and in a non-random contribution. The latter contribution is obtained treating each kind of contact as a reversible chemical reaction (quasichemical approximation). Guggenheim developed the theory for a lattice fluid system without holes and Panayiotou and Vera (PV) further improved it by introducing a compressible LF model accounting for the presence of hole sites [27]. In this model non-randomness of contacts between mers of the components of the mixture is assumed, but a random distribution of the holes is imposed (free volume random distribution hypothesis). Later, You et al. [28] and Panayiotou et al. [29] have extended this approach allowing for the non-randomness of all the possible couple of contacts, also including those involving the hole sites, still adopting a non-random quasichemical approximation.

More recently, Yeom et al. [30] and Panayiotou et al. [25,31–35] extended this non-randomness approach to include also the contribution of HB interactions, in a way similar to that adopted in the PS model to extend random LF approach. In the following we will refer to non-random model accounting for HB, proposed by the group of Panayiotou in Refs. [31,34], as ‘Non Random lattice fluid Hydrogen Bonding’ (NRHB) model.

A comparison of the capability of NRHB and of a simplified version of SAFT (i.e. Simplified Perturbed-Chain SAFT, sPC-SAFT) which includes an association term [36] in interpreting and correlating fluid phase equilibria in complex systems which exhibit specific interactions, has been reported by Tsivintzelis et al. [37,38]. According to these authors, NRHB and sPC-SAFT approaches, at least for the case mixtures of low molecular weight compounds, have proven to display similar performances in correlating and predicting phase equilibria in binary mixtures containing several types of associating fluids.

In the present contribution, water sorption behaviour in PCL is interpreted by using models based on the LF framework and including HB contribution, i.e. PS and NRHB approaches,

to account for specific HB interactions that can take place in PCL–water mixtures. In fact, water molecules can establish specific self-interactions between their proton donor and proton acceptor groups. These interactions can take place, as well, in the water vapour phase in equilibrium with the polymer–penetrant mixture. Furthermore, specific cross-interactions can occur in the water–polymer mixture between the proton donor groups of water molecules and the proton acceptor groups (i.e. ester linkages) present on the repeating unit of the polymer. Performances of PS [21] and NRHB [31,34] models have been compared to those of PS model without the HB contribution (referred to in the following simply as ‘LF model’) to interpret gravimetric sorption data.

The PS model has already been successfully used in the literature to investigate the phase behaviour of water–polymer systems, as is the case of water–polyethyleneglycol (PEG) mixtures [39]. Furthermore, the extension of the PS model to the case of network structures [35] has been used by Lele et al. [40] to calculate the swelling ratio of poly(*n*-isopropyl acrylamide) (PNIPA) in equilibrium with pure liquid water. Also NRHB has been used to describe vapour–liquid equilibria of binary polymer–solvent systems, where functional groups of the polymer can self-associate and cross-associate with the solvent molecules, providing a flexible approach for considering association in mixtures with complex hydrogen bonding behaviour. In particular, Tsivintzelis et al. [41] reported on the use of NRHB for the case of mixtures of poly(ethylene glycol), poly(propylene glycol), poly(vinyl alcohol) and poly(vinyl acetate) with several solvents, including water: NRHB provided in all cases good correlations of the experimental sorption isotherms.

It is important to note that all the models illustrated above, including those used in the present analysis to investigate the water sorption behaviour in PCL, are based on the LF framework which is suitable for totally amorphous rubbery polymers and does not account for the presence of crystalline domains. For the sake of interpretation of experimental water sorption isotherms in semicrystalline PCL, in the present contribution, crystals are modelled as being impervious and the overall solubility is predicted by rescaling the solubility of the pure amorphous phase to account for the presence of the crystalline fraction. The solubility in the amorphous phase is hence calculated using the approaches illustrated above, assuming that the presence of crystals does not alter the thermodynamic behaviour of the amorphous domains.

This approach could be questionable in view of possible effects of mechanical and mobility constraint exerted on the chains in the amorphous regions by the crystallites. In fact, a recent contribution by Morbidelli et al. [42] addresses the issue of modelling sorption thermodynamics of low molecular weight compounds in semi-crystalline polymers, by assuming that the crystalline phase is impervious to penetrants. The authors compare the efficacy of several approaches used in the modelling of thermodynamic behaviour of the amorphous regions. They compared the efficacy of three different approaches, each of them characterized by the following different features: (i) the behaviour of the amorphous phase in semicrystalline polymers can still be described by theories for solution thermodynamics developed for equilibrium rubbery polymers; (ii) the amorphous regions are constrained in their capability to attain the more compact equilibrium by the presence of crystallites and the amorphous regions are treated as glassy-like, out-of-equilibrium systems, adopting the theoretical framework developed to model sorption thermodynamics in glassy polymers (i.e. Non Equilibrium Lattice Fluid (NELF) theory) [43]; (iii) the crystallites act as chemical cross-linking junctions which limit the swelling of polymer matrix induced by the presence of penetrant and the semi-crystalline polymers are modelled as networked systems using a modification of standard lattice fluid theories for equilibrium systems, by adding an ‘elastic’ term [42,44]. In particular, the following models have been analysed and used

to model the behaviour of the amorphous phase: the equilibrium Sanchez–Lacombe (SL) and SAFT models were used to model the amorphous phase as a rubber polymer, the extension of SL to non-equilibrium glassy state (i.e. NELF model) was used to model the amorphous phase as a mobility restricted glassy polymer, and a modification of the SL model for cross-linked polymers was used to model the amorphous phase where crystals are imagined to act as cross-link junctions.

Morbidei et al. [42] came to the conclusion that the more relevant effect of crystalline domains on the behaviour of a rubbery amorphous phase is actually “[...] some sort of nonequilibrium effect caused by the rigidity, imparted to the rubbery portion of the polymers, by the presence of the crystallites” and the authors indicate that the overall interpretation of sorption thermodynamics of low molecular weight compounds in semicrystalline rubbery systems based on non-equilibrium approaches is the most appropriate since it supplies a more convincing qualitative overall physical picture of the whole set of experimental findings (i.e. solubility, swelling and values of partial molar volume of the penetrant). However, in the words of the authors, “[...] this approach is feasible only when reliable swelling data are available and this is the major limitation toward the use of such a model”.

More interestingly for the purposes of the present contribution, in the same paper it is underlined that, in terms of specific capability of estimating sorption isotherms, the approach based on an impervious crystalline phase and on an amorphous phase modelled simply using an equilibrium lattice fluid theory (SL), performs even better than the non-equilibrium approach under a quantitative view point. In fact, the authors conclude that, if swelling data are not available and hence it is not possible to use NELF model, both standard lattice fluid theories (in their case SL theory) and modified network lattice fluid theories [44] “exhibit comparable prediction ability when using the interaction parameter as an adjustable quantity”. These relevant indications reported in the paper by Morbidelli et al. [42] have been drawn on the basis of the analysis of sorption of CO₂ in several semicrystalline polymers. Although we are interested here in water sorption, the main general conclusions could be reasonably extended to the case at hand.

On the grounds of the results discussed above, in the present contribution it has been assumed that the only effect of the presence of crystalline domains is to limit the fraction of polymer mass accessible to water sorption, thus neglecting (i) the sorption capability of the crystalline domains of PCL, (ii) possible effects related to change in crystallinity induced by sorbed water and (iii) the effect of mechanical constraint exerted by crystals on the amorphous regions. Therefore, experimental data for overall water sorption of the semi-crystalline polymer have been simply scaled by accounting for the amount of the amorphous phase before comparison with predictions of lattice fluid EoS models, accounting or not for HB contribution.

2. Theoretical background

In this section, we review the more relevant features of the two lattice models accounting for HB contribution adopted to interpret water sorption isotherms in PCL. In particular, the main governing equations of the PS and of the NRHB models are briefly illustrated, referring for the full details to the original manuscripts and, in particular, to Ref. [21] for PS and Refs. [31,34] for NRHB.

In the following, it is addressed the specific case of a binary polymer–penetrant mixture at thermodynamic equilibrium with a pure vapour phase of the penetrant. It is assumed that the vapour phase is made of pure penetrant and does not contain any polymer

molecule. Subscript ‘1’ refers to penetrant and subscript ‘2’ refers to polymer.

2.1. PS model

The PS model consists in a lattice fluid theory where N molecules are assumed to be arranged on a compressible quasi lattice of N_r sites, N_0 of which are empty, with a lattice coordination number z (here assumed to be equal to 10). Each molecule of type i in the system occupies r_i sites of the quasi-lattice. Specific interaction forces and mean field forces are assumed to act separately, so that the configurational partition function associated to the system (i.e. pure penetrant vapour phase and polymer–penetrant mixture) can be factorized in a lattice fluid mean field contribution and a specific interaction (i.e. HB) contribution. Thus, each basic thermodynamic quantity can be expressed as the sum of a lattice fluid term and of an hydrogen bonding term: the lattice fluid contribution is expressed by a slightly modified version of the original SL theory [11], while the specific interaction term is expressed by using a combinatorial approach [25,34] based on Veystmann statistics [22,23]. In this section, it is illustrated the system of equations that, in the framework of the PS model, has been used to describe the phase equilibrium between a pure water vapour phase and a PCL–water mixture.

Occurrence of phase equilibrium between the binary polymer–penetrant mixture and the pure penetrant in vapour phase, implies the equality of the chemical potentials of penetrant in the two coexisting phases. The penetrant chemical potential in the polymer–penetrant mixture is expressed as the sum of a LF and a HB contribution [21]:

$$\mu_1 = \mu_{1,LF} + \mu_{1,H} \quad (1)$$

where

$$\begin{aligned} \frac{\mu_{1,LF}}{RT} = & \ln(\phi_1) + \left(1 - \frac{r_1}{r_2}\right) \phi_2 + r_1 \tilde{\rho} \theta_2^2 X_{12} \\ & + r_1 \left[\frac{-\tilde{\rho} + \tilde{P}_1 \tilde{v}}{\tilde{T}_1} + (\tilde{v} - 1) \ln(1 - \tilde{\rho}) + \frac{1}{r_1} \ln \left(\frac{\tilde{\rho}}{\omega_1} \right) \right] \end{aligned} \quad (2)$$

and

$$\frac{\mu_{1,H}}{RT} = r_1 v_H - \sum_i^m d_i^1 \ln \left(\frac{v_d^i}{v_{i0}} \right) - \sum_j^n a_j^1 \ln \left(\frac{v_a^j}{v_{0j}} \right) \quad (3)$$

Here the terms ϕ_i and θ_i represent, respectively, the ‘close packed’ volumetric fraction and the surface fraction of component i . $\tilde{P}_1 = P/P_1^*$ is the scaled pressure of penetrant (P is the pressure of the system and P_1^* is the characteristic pressure of penetrant), $\tilde{T}_1 = T/T_1^*$ is the scaled temperature of penetrant (T is the temperature of the system and T_1^* is the characteristic temperature of penetrant). Moreover, $\tilde{\rho} = \rho_{LF}/\rho^*$, where the scaling parameter ρ^* represents the close packed density of the mixture, while ρ_{LF} represents a kind of lattice fluid contribution to the density of the mixture and is defined as:

$$\rho_{LF} = \rho^* \left(\frac{rNv^*}{V_{LF}} \right) \quad (4)$$

where rN represents the total number of occupied cells, v^* is the ‘close-packed’ volume of an elementary cell of the system and V_{LF} is the lattice fluid contribution to the total volume. The parameter ω_1 in Eq. (2) represents the number of configurations available to a molecule of penetrant in the close-packed state and cancels out when equating the penetrant chemical potentials between two different phases at fixed pressure and temperature. Furthermore, X_{12} is defined as:

$$X_{12} = \frac{\varepsilon_{11}^* + (s_1/s_2)\varepsilon_{22}^* - 2(s_1/s_2)^{1/2}(1 - k_{12})(\varepsilon_{11}^* \varepsilon_{22}^*)^{1/2}}{RT} \quad (5)$$

in which R is the universal gas constant, k_{12} is the mean field lattice fluid interactional parameter which measures the departure from the geometric mean of the mixing rule for the characteristic energies of the lattice fluid, ε_{ij}^* represents the average mean field interaction energy per segment of molecule 'i' and s_i is the average number of LF contacts per segment (i.e. a surface to volume ratio characteristic of molecule i). Values for s_i can be calculated using UNIFAC procedure [45].

In Eq. (3) v_H represents the average number of hydrogen bonds per molecular segment and is defined as:

$$v_H = \sum_i^m \sum_j^n v_{ij} = \sum_i^m \sum_j^n \frac{N_{ij}}{rN} \quad (6)$$

In the previous expressions, N_{ij} is the total number of hydrogen bonding interactions between proton donor groups of type i and proton acceptor groups of type j and v_{ij} represents the average number per molecular segment of hydrogen bonding established between a proton donor of type i and a proton acceptor of type j . For the meaning of the other symbols in Eq. (3) see "List of symbols" or refer to the literature [21].

In the particular case of PCL–water system, the number of types of proton donors has been taken to be equal to 1 (i.e. $m = 1$): it corresponds to the H atoms in H_2O molecule. No donor groups are assumed to be present on the polymer backbone. The number of types of proton acceptors has been taken to be equal to 2 (i.e. $n = 2$) and they correspond, respectively, to the O atom on H_2O molecule (proton acceptor type 1) and to $-O-C=O$ group on polymer repeating unit (proton acceptor type 2).

Following the approach of Panayiotou [35], it has been assumed that the number of donor groups and the number of acceptor groups present on a water molecule are both equal to 2. Moreover, the number of proton acceptor groups per polymer repeating unit has been taken to be equal to 1 or 2. More on this in Section 4.2.

Based on the mentioned assumptions, in the case at hand we have self-hydrogen bonding only between water molecules, occurring both in the pure water vapour and in the polymer–water mixture, in a number equal, respectively, to N_{11}^V and N_{11}^{WP} and we have water–polymer cross-hydrogen bonding in the polymer–water mixture, in a number equal to N_{12}^{WP} .

The expression of the chemical potential of pure penetrant in vapour phase can be formally obtained by imposing that the 'close packed' volumetric fraction of penetrant is equal to 1, i.e. $\phi_1 = 1$, in Eq. (2) and by properly modifying the summation terms in Eqs. (3) and (6), by referring only to the acceptor and donor groups present on the penetrant molecule.

To model phase equilibrium, EoSs for both the pure vapour phase and for the polymer mixture have to be coupled with the expression stating the equality of penetrant chemical potentials in the two phases. The EoS expressions, obtained by minimizing Gibbs energy as a function of number of holes, are formally identical for the pure vapour phase and for the polymer–water phase and take the form:

$$\tilde{p}^2 + \tilde{P} + \tilde{T} \left[\ln(1 - \tilde{\rho}) + \tilde{\rho} \left(1 - \frac{1}{r} + v_H \right) \right] \quad (7)$$

\tilde{P} and \tilde{T} are defined, respectively as the ratio of pressure and temperature of the system with the scaling pressures and temperatures of the pure components or of the mixture. The procedure used to calculate the scaling parameters for mixtures is detailed in Ref. [21]. When Eq. (7) is referred to a pure component, r represents the number of cells occupied by one molecule of species i and is also indicated as r_i , while, in the case of a mixture, the value of r , which represents the average number of cells occupied by a molecule in the lattice, is obtained as molar average of r_i s.

Finally, in order to close the problem, one needs to couple another set of equations, defined for each of the phases at equilibrium, relating the lattice fluid reduced density contribution $\tilde{\rho}$ for each phase to v_{ij} . These equations are obtained by minimizing the Gibbs energy as a function of the number of each type of hydrogen bonding interactions and have the following form:

$$\frac{v_{ij}}{v_{i0}v_{j0}} = \tilde{\rho} \exp \left(-\frac{G_{ij}^0}{RT} \right), \quad \text{for all } (i, j) \quad (8)$$

where v_{i0} represents the average number of unbonded proton donor of type i per molecular segment and v_{j0} represents the average number of unbonded proton acceptor of type j per molecular segment, while G_{ij}^0 is expressed as:

$$G_{ij}^0 = E_{ij}^0 - T \cdot S_{ij}^0 + P \cdot V_{ij}^0 \quad (9)$$

Here G_{ij}^0 , E_{ij}^0 , S_{ij}^0 and V_{ij}^0 represent, respectively, the molar Gibbs energy of formation, the molar internal energy of formation, the molar entropy of formation and the molar volume of formation associated to hydrogen bonding between the proton donor group of type i and the proton acceptor group of type j . As for the volume change associated to the formation of a water–water self-HB, the values of G_{11}^0 , E_{11}^0 and S_{11}^0 are the same both in the vapour and in the polymer mixture phase. In the present context, V_{12}^0 has been assumed to be equal to zero. In fact, in Eq. (9) it is multiplied by the system pressure, that has very low values in the case at hand, thus contributing a term which is orders of magnitude lower than the other terms in the expression. The assumption $V_{12}^0 = 0$ is somewhat relevant only if one is interested in the exact prediction of the volume of the system, but does not affect to any significant degree the calculations performed here. Two cases are instead considered for V_{11}^0 , one in which it is imposed that $V_{11}^0 = 0$ and one in which $V_{11}^0 \neq 0$, its value being taken from literature [40].

In summary, the PS model consists in the following set of equations to be solved to determine the penetrant solubility in a rubbery polymer:

- Equality of chemical potentials of penetrant in the two phases.
- Equations of state for the vapour and for the polymer mixture phases (see Eq. (7)).
- Equations for the number of different hydrogen bonds established in the two phases at equilibrium (see Eq. (8)).

Solution of this system of equations supplies, at fixed values of pressure and temperature, the density of the two phases, the concentration of penetrant in the polymer–penetrant mixture and the number of each type of hydrogen bonds in the two phases (i.e. N_{11}^V , N_{11}^{WP} and N_{12}^{WP}). This model has been used to fit experimental sorption isotherms of water in PCL, assuming as fitting parameters k_{12} , E_{12}^0 and S_{12}^0 .

Lattice fluid scaling parameters for PCL (i.e. T_2^* , P_2^* and ρ_2^*) have been determined by independent fitting of PVT data for PCL using Eq. (7) (setting $v_H = 0$, since no self-hydrogen bonding is assumed to occur between groups located on the polymer backbone). In the case in which we have imposed $V_{11}^0 = 0$, lattice fluid scaling parameters for water (i.e. T_1^* , P_1^* and ρ_1^*), and self-HB parameters (i.e. E_{11}^0 and S_{11}^0) have been determined by simultaneous fitting of literature data for density of the pure vapour and liquid water phases at equilibrium and of literature data for equilibrium water vapour pressure [46]. To this aim, it has been used the set consisting of the equality of water chemical potentials, of Eq. (7) and of Eq. (8), as specialized for the case of phase equilibrium of pure water. Conversely, in the case in which it has been taken $V_{11}^0 \neq 0$, scaling parameters and HB parameters, including V_{11}^0 , have been taken from the literature [40].

The formulation of PS model for the case in which no hydrogen bonding contribution is assumed to occur, and hence accounting only for mean field interactions, is referred to here as 'LF model' and is very close to the original lattice fluid model proposed by Sanchez and Lacombe [11]. In the following, when LF model is used, the only fitting parameter needed in interpreting sorption isotherms is k_{12} . PCL scaling parameters are identical to those used for the PS model and the water scaling parameters can be taken from the literature value reported in the case of SL model [11], since their numerical values are the same both for the PS model without HB contribution and for SL model.

2.2. NRHB model

In this section, it is briefly illustrated the system of equations that, in the framework of the NRHB model, have been used to describe the phase equilibrium between pure water vapour phase and a PCL–water mixture.

As already anticipated, NRHB model differs from PS model only in the lattice fluid contribution and, in the following, we will focus only on this term. In particular, in contrast to the PS model, NRHB model accounts for non-randomness of lattice fluid contacts [34]. The scaling parameters differ from the case of PS: the first two scaling parameters are ε_h^* and ε_s^* and are needed for the calculation of the mean interaction energy per mole of segment of component i , ε_{ii}^* . The third scaling parameter is $\nu_{sp,0}^*$ and is used for the calculation of the close packed density $\rho^* = 1/\nu_{sp}^*$, as by the following equation:

$$\nu_{sp}^* = \nu_{sp,0}^* + (T - 298.15)\nu_{sp,1}^* \quad (10a)$$

Here ν_{sp}^* is expressed in $\text{cm}^3 \text{g}^{-1}$. In the case one deals with a polymer, Eq. (10a) takes the form:

$$\nu_{sp}^* = \nu_{sp,0}^* + (T - 298.15)\nu_{sp,1}^* - 0.135 \times 10^{-3} \times P \quad (10b)$$

where P is expressed in MPa. In Eqs. (10a) and (10b) $\nu_{sp,1}^*$ is treated as a characteristic parameter for a given homologous series and values are reported in the literature [41]. For the specific case of water it is taken to be equal to $-0.3 \times 10^{-3} \text{cm}^3 \text{g}^{-1} \text{K}^{-1}$ while in the case of PCL it is taken to be equal to $0.150 \times 10^{-3} \text{cm}^3 \text{g}^{-1} \text{K}^{-1}$.

The value of r_i can be obtained by the following expression:

$$r_i = \frac{(M.W.)_i \nu_{sp}^*}{\nu^*} \quad (11)$$

where $M.W.$ and ν_{sp}^* stand for molecular weight of component i . Differently from PS, the hard-core volume per segment, ν^* , is assumed to be the same for all fluids and equal to $9.75 \text{cm}^3 \text{mol}^{-1}$ [31]. As for PS model, the shape factor, s_i , defined as the ratio of molecular surface to molecular volume, $s_i = zq_i/zr_i = q_i/r_i$, can be calculated from UNIFAC group contribution method [31].

For binary mixtures the following mixing rules are used:

$$\varepsilon^* = \sum_{i=1}^2 \sum_{j=1}^2 \theta_i \theta_j \varepsilon_{ij}^* \quad (12)$$

where

$$\varepsilon_{12}^* = (1 - k_{12}) \sqrt{\varepsilon_{11}^* \varepsilon_{22}^*} \quad (13)$$

The resulting expressions of the equation of state and of the chemical potential of component 1 in a binary mixture, are respectively represented [34] by Eqs. (14) and (15):

$$\bar{p} + \bar{T} \left[\ln(1 - \bar{\rho}) - \bar{\rho} \left(\sum_{i=1}^2 \phi_i \frac{l_i}{r_i} - \nu_H \right) - \frac{z}{2} \ln \left(1 - \bar{\rho} + \frac{q}{r} \bar{\rho} \right) + \frac{z}{2} \ln \Gamma_{00} \right] = 0 \quad (14)$$

$$\begin{aligned} \frac{\mu_1}{RT} = & \ln \frac{\phi_1}{\omega_1 r_1} - r_1 \sum_{j=1}^2 \frac{\phi_j l_j}{r_j} + \ln \bar{p} + r_1 (\bar{\nu} - 1) \ln(1 - \bar{\rho}) \\ & - \frac{z}{2} r_1 \left[\bar{\nu} - 1 + \frac{q_1}{r_1} \right] \ln \left[1 - \bar{\rho} + \frac{q}{r} \bar{\rho} \right] \\ & + \frac{z q_1}{2} \left[\ln \Gamma_{11} + \frac{r_1}{q_1} (\bar{\nu} - 1) \ln \Gamma_{00} \right] + r_1 \frac{\bar{p} \bar{\nu}}{\bar{T}} - \frac{q_1}{\bar{T}_1} + \frac{\mu_{1,H}}{RT} \end{aligned} \quad (15)$$

The corresponding expressions of the EoS and of the chemical potential for the pure component 1 (i.e. the penetrant) can be obtained from Eqs. (14) and (15) by setting $\phi_1 = 1$ and the number of components in the summation equal to 1. In Eqs. (14) and (15) l_i is a dimensionless parameter defined in Ref. [34].

In Eq. (15) ω_1 is a characteristic quantity for the penetrant and, as for PS model, takes into account the flexibility and the symmetry of the molecule. As already mentioned, this parameter cancels out in all equilibrium calculations of interest here. The state variables Γ_{00} and Γ_{11} are non-random factors for the distribution, respectively, of an empty site around another empty site and of molecular segments of penetrant around a molecular segment of the penetrant itself. Their values can be obtained by solving a set of equations, which we do not report here for the sake of brevity (see for details Ref. [34]), obtained by minimizing Gibbs energy as a function of number of different kinds of lattice fluid contacts and by imposing material balance expressions for the lattice fluid contacts. These equations do not introduce any new unknown parameter and are coupled with EoS equations and expressions for chemical potentials. The characteristic temperature, T^* , and pressure, P^* , are related to the mean inter-segmental energy, ε^* , by:

$$\varepsilon^* = RT^* = P^* \nu^* \quad (16)$$

The HB contributions, i.e. ν_H in the EoS expression (Eq. (14)) and $\mu_{1,H}/RT$ in the expression of penetrant chemical potential (Eq. (15)), are identical to the case of PS model and are not reported again here. It is worth of note that, in applying the NRHB approach for interpreting water sorption isotherms in PCL, we have imposed $V_{11}^0 = 0$, according to the assumption made by the authors of NRHB in recent publications [41]. As suggested in the same paper [41] and as already done in the case of PS, we have also assumed that $V_{12}^0 = 0$. Moreover, as for PS model, the values of G_{11}^0 , E_{11}^0 and S_{11}^0 have been taken to be the same both in the vapour and in the polymer mixture phase.

In summary, the set of equations to be solved to determine the water solubility in PCL according to the NRHB model are as follows:

- Equivalence of chemical potentials of penetrant in the two phases.
- Equations of state for the vapour and for the polymer mixture phases (see Eq. (14)).
- Equations for the number of hydrogen bonds establishing in the two phases at equilibrium (see Eq. (8)).
- Equations for Γ_{00} and Γ_{11} state variables in the two phases (see Ref. [34]).

Solution of this system of equations supplies, at fixed values of pressure and temperature, the density of the two phases, the

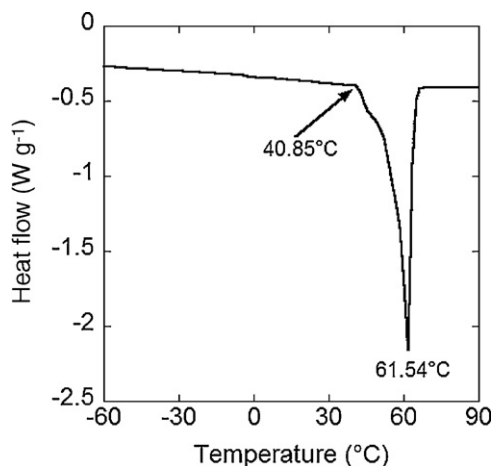


Fig. 1. DSC scan of PCL – melting onset temperature (40.85 °C) and melting peak temperature (61.54 °C) are indicated.

concentration of penetrant in the polymer–penetrant mixtures, the number of each type of hydrogen bonds in the two phases (i.e. N_{11}^V , N_{11}^{WP} and N_{12}^{WP}) and the values of Γ_{00} and Γ_{11} parameters in the two phases. This model has been used to fit experimental sorption isotherms of water in PCL, assuming as fitting parameters k_{12} , E_{12}^0 and S_{12}^0 .

Lattice fluid scaling parameters for pure PCL (i.e. ε_{h2}^* , ε_{s2}^* and $\nu_{sp,02}^*$) have been determined by independent fitting of PVT data for PCL using Eq. (14) (setting $\nu_H = 0$, since no self-hydrogen bonding is assumed to occur between groups located on the polymer backbone). Lattice fluid scaling parameters for water (i.e. ε_{h1}^* , ε_{s1}^* and $\nu_{sp,01}^*$), E_{11}^0 and S_{11}^0 have been taken from the literature [41].

3. Materials and methods

3.1. Materials

A film grade thermoplastic PCL, CAPA® FB100, was used, supplied by Solvay Warrington (Cheshire, WA4 6HB, United Kingdom). The material was supplied as a 100% resin in the form of 3 mm pellets. The mean molecular weight is $M_w = 80,000$. The material has been processed by using a film blowing equipment obtaining a film with a thickness of around 45 μm . Film blowing was performed on a lab scale equipment (Collin E 20T, Germany). The temperatures of the four heating sections of the extruder barrel and of the die (80/100/120/110/110), the velocity of the take-off rolls and the volume of the bubble were adjusted in order to achieve a stable bubble. The screw speed was set at 40 rpm.

3.2. Thermal analysis

Differential scanning calorimetry (DSC) was conducted using a Q1000 calorimeter by TA Instruments (New Castle Delaware, USA) to study the thermal properties of PCL. The heating scan was performed under temperature with a heating rate of $10^\circ\text{C min}^{-1}$, between -80 and 100°C . Tests were performed under nitrogen atmosphere in a non-hermetic aluminum pan. Each measurement has been duplicated.

The PCL calorimetric scan (see Fig. 1) displays an endothermic peak in the range between 50 and 80°C , with an onset of melting located at around 40.8°C , with a melting temperature, T_m , equal to 61.54°C and with an enthalpy of melting, ΔH_m , equal to 78.77 J g^{-1} .

The weight percent crystallinity of the PCL sample, χ_C , was estimated to be equal to 58.2% by using the equation:

$$\chi_C = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad (17)$$

where the enthalpy of melting per gram of a pure crystal of PCL, ΔH_m^0 , has been taken to be equal to 135.31 J g^{-1} , according to data available in the literature [47].

3.3. Water vapour sorption isotherms

Water vapour sorption isotherms were determined using a Q5000 SA automatic microbalance by TA Instruments (New Castle Delaware, USA) which has a nominal weight range of 0.1 g, a sensitivity better than 10^{-7} g and a signal resolution equal to 10^{-8} g . The microbalance can operate in the temperature range 5 – 85°C under a flux of nitrogen at atmospheric pressure humidified at an automatically controlled preset value of humidity. The relative humidity control range is 0 – 98% with a control accuracy equal to $\pm 1\%$.

Before each sorption analysis, samples were dried at the test temperature until a constant weight was obtained. Sorption isotherms were determined at 298, 303 and 310 K and, at each temperature, tests were performed at six values of relative humidity ranging from 0.15 to 0.85. The highest value of test temperature (310 K) was chosen to be lower than the one of melting onset (313.8 K), to avoid even slight decrease of the starting crystallinity. The humidity was increased stepwise after having reached sorption equilibrium in the previous step. Detection of equilibrium was automatically performed by the instrument according to a user defined threshold of relative weight change. Experimental analyses were performed at each temperature on a virgin sample. Each sorption isotherm was performed twice on the same sample verifying that data were repeatable, thus confirming that contact with water at highest activity did not modify the polymer structure.

Sorption data obtained for semi-crystalline PCL were re-elaborated to rescale the sorbed values with respect to the amorphous fractions, by assuming that water is not soluble in the crystalline phase. In details, the experimental mass fraction of water (w_1^{tot}) referred to the total mass of polymer is given by:

$$w_1^{tot} = \frac{m_1}{m_1 + m_2^{am} + m_2^{cry}} \quad (18)$$

The mass fraction of water referred only to the amorphous phase of polymer, w_1^{am} , which is defined as:

$$w_1^{am} = \frac{m_1}{m_1 + m_2^{am}} \quad (19)$$

can be calculated by rescaling the experimentally determined w_1^{tot} according to the following equation:

$$w_1^{am} = \left(1 + w^{am} \left(\frac{1}{w_1^{tot} - 1} \right) \right)^{-1} \quad (20)$$

In the previous expressions, m_1 is the mass of water, m_2^{am} the mass of amorphous phase of pure PCL, m_2^{cry} the mass of crystalline phase of pure PCL, $w^{am} = m_2^{am} / (m_2^{am} + m_2^{cry})$ is the mass fraction of amorphous phase in the pure polymer. w_1^{am} can be readily converted into the corresponding volumetric fraction ϕ_1^{am} according to the corresponding lattice fluid definitions [13,21,34].

It is worth noticing that, in performing these calculations, it has been assumed that the amount of crystalline phase is not affected by sorbed water.

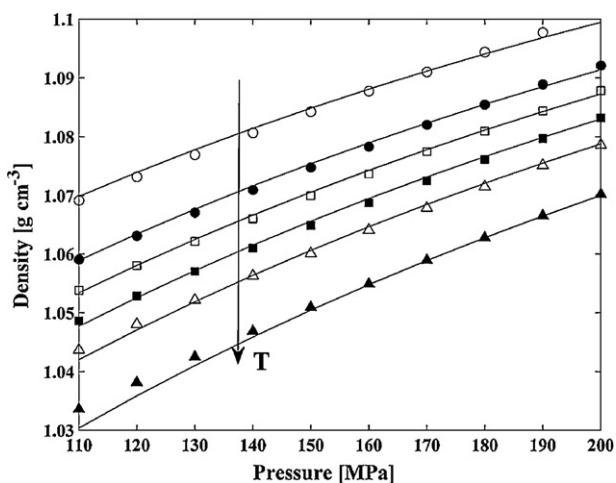


Fig. 2. Fitting of PVT data for PCL by using LF model. The arrow indicates the increasing direction of temperature. Marker symbols for data determined at six temperatures are, respectively, 400 K (○), 421 K (●), 431 K (□), 441 K (■), 451 K (△) and 471 K (▲). The lines represent the theoretical results. Best fitting parameters are reported in Table 1.

3.4. PVT behaviour of PCL

In order to evaluate the EoS parameters for pure PCL, the PVT behaviour of PCL has been evaluated using a GNOMIX high pressure dilatometer (Boulder, CO, USA). This instrument is based on the well-established bellows technique, in which a hydrostatic pressure is applied to a sample of known volume in correspondence of the starting pressure and temperature of the test, through a confining fluid (mercury). In this way, volume changes of the sample are measured by a linear variable differential transformer mounted beneath the pressure vessel. This technique is described in detail in Ref. [48]. Since the dilatometer provides only measurements of volume change, the knowledge of polymer density at known pressure and temperature conditions is needed. To this aim, density of PCL was evaluated at 25 °C and 1 atm using a gas pycnometer (Micromeritics Accupyc 1342).

The PVT behaviour has been determined by using isothermal compressions procedure (defined as ‘ITS runs’ on GNOMIX software), which has been performed up to a pressure of 200 MPa (in 10 MPa steps) and in the 25–200 °C (10 °C steps) temperature range.

4. Results and discussion

4.1. Interpretation of water sorption isotherms in PCL using LF model

As already detailed in the theoretical background section, the LF model corresponds exactly to the PS model without the HB contribution. It is a purely lattice fluid theory with no terms accounting for self- and cross-hydrogen bonding. We first illustrate here the capability of LF model to interpret sorption isotherms of water vapor in PCL. Sections 4.2 and 4.3 will be then respectively focused on PS and NRHB models.

Scaling parameters for PCL have been obtained by fitting experimental PVT data with pure fluid LF equation of state. Data fitting has been performed using a Levenberg–Marquardt minimization algorithm which operates by comparing experimental densities with those predicted theoretically, which have been calculated by using a Newton–Raphson method to solve model equations for equilibrium density. In Fig. 2 are reported the density–pressure experimental isotherms for pure PCL at the molten state which have been measured at six different temperatures. The three scaling

Table 1

LF EoS parameters for pure components (PCL and water). T^* , P^* and ρ^* for PCL have been obtained by fitting PVT data using LF model for pure fluids. T^* , P^* and ρ^* for water have been taken from the literature [11]. The values of s , both for PCL and water, are taken from the literature [31], calculated using group contribution calculation scheme UNIFAC [45].

Component	T_i^* [K]	P_i^* [MPa]	ρ_i^* [g cm ⁻³]	s
PCL	594 ± 10	468 ± 10	1.163 ± 1 × 10 ⁻³	0.818
Water	623.0	2687.1	1.105	0.861

parameters for PCL (T_2^* , P_2^* and ρ_2^*) have been determined by performing a simultaneous fitting of all the isotherms and fitting lines corresponding to the optimized parameters are reported in Fig. 2 as well.

The values of corresponding LF model parameters for pure water were taken from the literature referred to the classical Sanchez–Lacombe (SL) EoS theory for pure fluids [11], since the forms of SL and LF model EoS are identical for the case of pure fluids. The values of the three independent scaling parameters for water and PCL, i.e. the characteristic temperatures (T_1^* and T_2^*), the characteristic pressures (P_1^* and P_2^*) and the characteristic densities (ρ_1^* and ρ_2^*), are reported in Table 1. In the same table are also reported the values of the surface to volume ratio characteristic of each molecule. This parameter, as already pointed out, has been taken from the literature [31] and its value is the result of the UNIFAC group contribution calculation scheme [45].

LF model has been then used to fit water sorption isotherms in the amorphous phase of PCL (see Fig. 3). As detailed in the experimental section, isotherms data points reported in Fig. 3 are referred to the water mass fraction in the amorphous phase of PCL, as calculated after proper re-scaling of data obtained for the semi-crystalline polymer. This same set of data has been used to test all the models discussed in this work. The amorphous phase mass fraction used for the data normalization was equal to 0.418. The accuracy of water solubility data in the amorphous phase determined by this procedure, as already discussed, obviously rests on the hypothesis that an actually negligible amount of water is absorbed in the crystalline domains and that the amount of crystalline phase is unaffected by water sorption.

The scaled experimental sorption isotherms have been fitted with LF model for fluid mixtures using as fitting parameter only k_{12} (optimized value is reported in Table 3). Data fitting has been performed using a Levenberg–Marquardt minimization algorithm which operates by comparing experimental sorption data with

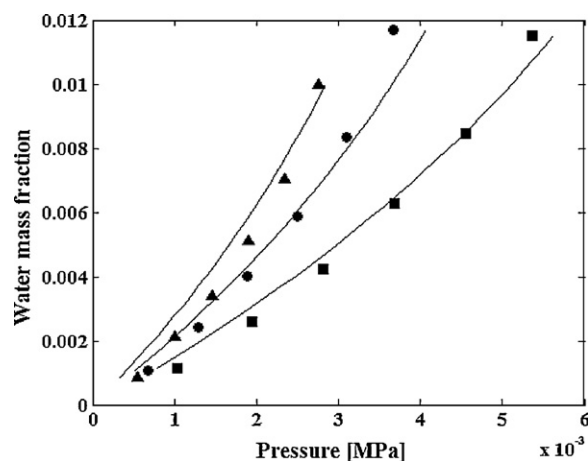


Fig. 3. Fitting of water sorption isotherms in PCL by using LF model. Model fitting is represented by continuous lines. Water mass fraction refers to the amorphous phase of PCL. Marker symbols for data obtained at three temperatures are, respectively, 298 K (▲), 303 K (●) and 310 K (■). The fitting parameter, k_{12} , is reported in Table 3.

Table 2
PS EoS parameters for pure components (PCL and water). T^* , P^* and ρ^* for PCL have been obtained by fitting PVT data using PS model for pure fluids. T^* , P^* , ρ^* , E_{11}^0 and S_{11}^0 for water have been obtained by fitting of vapour–liquid equilibrium data, taken from Ref. [46], using PS theory for pure fluids, for the case in which it was assumed $V_{11}^0 = 0$. In the case in which $V_{11}^0 \neq 0$ was assumed, the parameters T^* , P^* , ρ^* , E_{11}^0 , S_{11}^0 and V_{11}^0 for water were taken from the literature [40]. The values of s , both for PCL and water, are taken from the literature [31] where they have been calculated using group contribution calculation scheme UNIFAC [45].

Component	T_i^* [K]	P_i^* [MPa]	ρ_i^* [g cm ⁻³]	E_{11}^0 [J mol ⁻¹]	S_{11}^0 [J mol ⁻¹ K ⁻¹]	s	V_{11}^0 [cm ³ mol ⁻¹]
PCL	594 ± 10	468 ± 10	1.163 ± 1 × 10 ⁻³	–	–	0.818	–
Water	484 ± 10	453 ± 10	1.065 ± 1 × 10 ⁻³	–18,424 ± 200	–19.8 ± 0.1	0.861	0
Water	518	475	0.853	–15,500	–16.6	0.861	–4.2

those predicted theoretically, which have been calculated by using a Newton–Raphson method to solve model equations for water concentration. This procedure has been adopted also when using PS and NRHB models.

As can be appreciated LF model results in a fitting which is not completely satisfactory in the whole activity range, likely due to the fact that this model is intrinsically unable to account for interactions by hydrogen bonding.

4.2. Interpretation of sorption isotherms using PS model

The PS model, which is able to explicitly account for possible PCL–water and water–water hydrogen bond interactions, is expected to display an improved capability of correctly interpreting water sorption thermodynamics in PCL. In fact this theory, as compared to LF model, introduces an additive contribution to the Gibbs energy of the mixture related to self- and cross-hydrogen bonding occurring in the mixture. The PS model still retains the random nature of site contacts in the lattice, despite the fact that the presence of specific interactions affects the reliability of this hypothesis.

In view of the structure of the model for pure fluids and of the fact that no self-hydrogen bonding is expected for pure PCL, the scaling parameters for PCL are the same as those adopted for LF model. In the case of water self-association by HB two cases have been considered, i.e. $V_{11}^0 = 0$ and $V_{11}^0 \neq 0$. In the first case, calculation of the values of the parameters, i.e. the three lattice fluid scaling parameters (T_1^* , P_1^* and ρ_1^*) and the two parameters related to water self-hydrogen bond formation (i.e. E_{11}^0 and S_{11}^0), has been performed by simultaneously fitting (see Section 2) data for equilibrium water vapour pressure and for densities of the vapour and of the liquid phases at equilibrium [46]. As suggested by Panayiotou [34], hydrogen bonding interactions between water molecules have been modelled assuming two equivalent proton donor groups and two equivalent proton acceptor groups for each molecule. The fitting has been performed in a range of temperatures and pressures well below the critical point, since the mean field approach implemented by the PS theory is not suited to describe the behaviour of systems near the critical point [7].

As evident in Fig. 4, the model supplies an accurate fitting over the entire temperature range considered. The values obtained for the fitting parameters are reported in Table 2. The values for s_i are the same as for the case of LF model since they are independent on the adopted model.

In the case of $V_{11}^0 \neq 0$, parameters were already available in the literature [40] and are reported as well in Table 2. It is worth noting that literature values are again based on the assumption that on each water molecule there are two equivalent proton donor groups and two equivalent proton acceptor groups.

PS model has been then used to interpret water sorption isotherms in amorphous PCL. Preliminary FTIR analyses point to the occurrence of two species of sorbed water, one establishing self-HB interactions and one establishing HB with the carbonyl group of PCL, although water interaction with the ether group cannot be presently ruled out. These findings were used in the formulation of

the model to select the types and number of proton acceptor and proton donor groups involved in HB.

In particular, it has been assumed that only water molecules are capable of forming self-HB and the same number of proton acceptor and proton donor groups per molecule has been adopted as for the case of pure water. As already mentioned, the energy and entropy of formation of self-HB, i.e. E_{11}^0 , S_{11}^0 and V_{11}^0 have been taken, according to the original model [24], to have the same values in the mixture as for the case of pure water.

Concerning cross-HB interactions, it has been assumed that the two proton donor groups present on each water molecule interact with proton acceptor groups located on the polymer backbone. Two cases have been considered, differing in the number of proton acceptor groups per polymer repeating unit. In the first case, one proton acceptor is considered, identifying it with the carbonyl group. In the second case, two proton acceptors are considered, respectively the carbonyl and the ether groups. In both cases, three fitting parameters are present, i.e. the mean field PCL–water interaction parameter, k_{12} , the internal energy of formation of PCL–water HB interaction, E_{12}^0 , and the entropy of formation of PCL–water HB interaction S_{12}^0 . In fact, in the case of two proton acceptor groups per repeating unit of PCL, E_{12}^0 and S_{12}^0 parameters represent average values between the two different proton acceptors (carbonyl and ether groups). This approach has been adopted in order to limit the number of fitting parameters to three also in the case where two proton acceptor groups per polymer repeating units are assumed. Based on the arguments [41] already invoked in the section on theoretical background, the volume change associated to formation of cross-hydrogen bonds, V_{12}^0 , has been imposed to be zero.

PS model has been applied in the two different cases $V_{11}^0 = 0$ and $V_{11}^0 \neq 0$: in both cases the model exhibits a very good fitting capability of the sorption isotherms. The quality of fitting is the same both in the case of two proton acceptor groups per repeating unit as

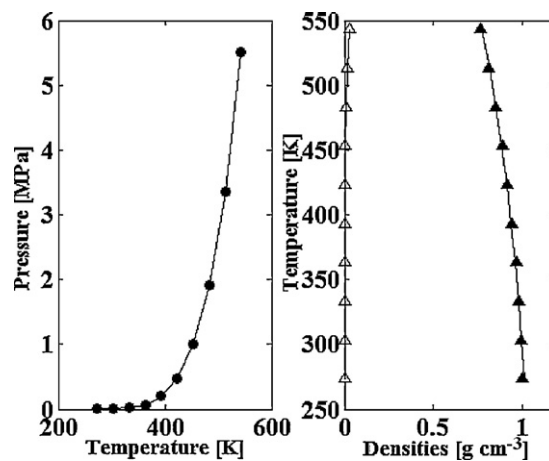


Fig. 4. Determination of PS model parameters for pure water. Model fitting (continuous lines) of literature data [46] for water vapor pressure (left) and water liquid and vapor densities (right) at liquid–vapor equilibrium. Best fitting parameters are reported in Table 2.

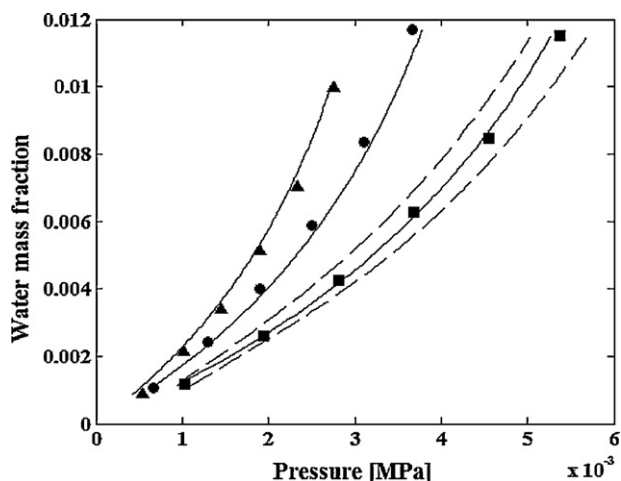


Fig. 5. Fitting of water sorption isotherms in PCL by using PS model. The case of two proton acceptor groups per repeating unit of PCL and $V_{11}^0 = 0$ is reported. Model fitting is represented by continuous lines. Water mass fraction is referred to the amorphous phase of PCL. Marker symbols for data obtained at three temperatures are, respectively, 298 K (\blacktriangle), 303 K (\bullet) and 310 K (\blacksquare). Fitting parameters are reported in Table 3. Dashed lines represent statistical bounds for predicted 310 K isotherm.

well as in the case of one proton acceptor group per repeating unit of PCL. As an example, in Fig. 5 is reported the case of PS model with $V_{11}^0 = 0$ and two proton acceptors. Results of fitting with PS model are considerably better than in the case of LF model, thus indicating that the occurrence of HB in the systems has to be accounted for to obtain reliable interpretation of water sorption thermodynamics in PCL.

The best fitting values of the three parameters for the two cases of application of PS model are reported in Table 3. For the $V_{11}^0 = 0$ assumption, the values determined for E_{12}^0 for one and two proton acceptor groups per repeating unit of polymer are very close to each other and appear to be in the range of values generally expected for hydrogen bonding interactions [41]. Values for E_{12}^0 obtained in the case of the $V_{11}^0 \neq 0$ assumption are very close to the ones obtained in the case of the $V_{11}^0 = 0$ assumption. Further, the values of S_{12}^0 obtained in the $V_{11}^0 = 0$ and in the $V_{11}^0 \neq 0$ cases, are quite different when the assumption one and two proton acceptor groups per repeating unit are compared. Moreover, greater values for S_{12}^0 have been obtained in the case of the $V_{11}^0 \neq 0$ assumption as compared to calculations performed in the case of the $V_{11}^0 = 0$ assumption.

Values of parameters in Table 3 are reported indicating also the 95% confidence intervals estimated through Jacobian analysis in correspondence of the set of optimized fitting parameters. As a consequence of the statistical uncertainty of parameters values, the resulting predicted isotherms are actually estimates. In Fig. 5 this uncertainty of the model prediction is represented graphically in the form of two bounds (dashed curves) for the isotherm at 310 K (for the sake of clarity the same representation for the other isotherms has been omitted) for the case of $V_{11}^0 = 0$. These bounds have been evaluated by perturbing the estimated fitting parameters within the confidence intervals. The analysis indicates that,

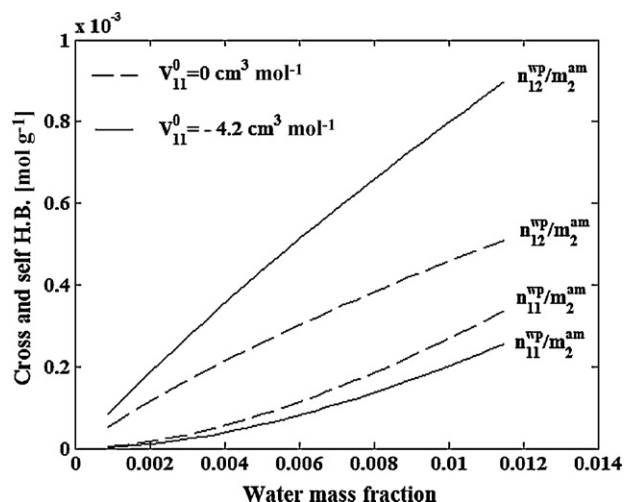


Fig. 6. Predicted values of water self-HB and water–polymer cross-HB in terms of moles of established hydrogen bonds, in the PCL–water mixture, per gram of amorphous dry polymer as a function of water mass fraction. Predictions performed by using PS with $V_{11}^0 = 0$ and $V_{11}^0 \neq 0$ for the case of two proton acceptor groups and $T = 298$ K.

although the range of investigated temperatures is rather limited, the reliability of the set of estimated parameters is satisfactory. The same conclusion also applies for the case of $V_{11}^0 \neq 0$.

Experimental FTIR in situ analysis of water sorption in PCL is in progress in order to directly obtain the values of entropies and energies of HB formation from elaboration of vibrational spectra, thus reducing considerably the number of fitting parameters.

Once the optimized parameters have been determined by the fitting procedure, PS model has been used to predict the amounts of self-HB (i.e. 1–1) cross-HB (i.e. 1–2) interactions forming in the PCL–water mixture. In Fig. 6 are reported, as an example, the predictions of calculations performed in the case of two proton acceptor groups per repeating unit for the cases $V_{11}^0 = 0$ and $V_{11}^0 \neq 0$ at $T = 298$ K. In details, the moles of self-HB occurring between the proton donor and the proton acceptor groups of water molecules present in the water–PCL mixture, normalized per mass of amorphous phase of PCL (i.e. n_{11}^{wp}/m_2^{am}) and the moles of cross-HB occurring between the proton donor groups of water molecules and the proton acceptor groups present on PCL backbone, normalized per mass of amorphous phase of PCL (i.e. n_{12}^{wp}/m_2^{am}), are both reported as a function of water mass fraction in the amorphous phase of PCL.

As it is evident, the concentration of self-HB displays an upward concavity, reflecting the clustering tendency of water molecules as water concentration increases. The model predicts (results not shown) that self-association decreases with increasing the temperature, as expected for exothermic processes. Predictions obtained imposing $V_{11}^0 = 0$ are quantitatively and qualitatively close to those obtained for the case $V_{11}^0 \neq 0$.

As opposed to self-HB, the concentration of cross-HB increases with water concentration displaying a downward concavity. This behaviour reflects the tendency to approach a saturation level of

Table 3

LF and PS mean field interaction parameters and PS cross-HB parameters for the PCL–water system, as obtained from data fitting of experimental sorption isotherms.

Model	Proton acceptors per PCL repeating unit	k_{12}	E_{12}^0 [J mol ⁻¹]	S_{12}^0 [J mol ⁻¹ K ⁻¹]	V_{12}^0 [cm ³ mol ⁻¹]
LF	–	0.0619 ± 10^{-3}	–	–	–
PS	1	-0.0900 ± 10^{-3}	$-13,230 \pm 100$	-10.17 ± 0.1	0
PS	2	-0.0620 ± 10^{-3}	$-13,521 \pm 100$	-16.02 ± 0.1	0
PS with $V_{11}^0 \neq 0$	1	-0.1876 ± 10^{-3}	$-13,500 \pm 100$	-19.27 ± 0.1	0
PS with $V_{11}^0 \neq 0$	2	-0.1742 ± 10^{-3}	$-13,400 \pm 100$	-24.07 ± 0.1	0

Table 4
NRHB EoS parameters for pure components (PCL and water). ε_h^* , ε_s^* and $v_{sp,0}^*$ for PCL have been obtained by fitting PVT data using NRHB model for pure fluids. ε_h^* , ε_s^* , $v_{sp,0}^*$, E_{11}^0 and S_{11}^0 for water have been taken from the literature [41]. The values of s , both for PCL and water, are taken from the literature [31], where they have been calculated using group contribution calculation scheme UNIFAC [45].

Component	ε_h^* [J mol ⁻¹]	ε_s^* [J mol ⁻¹ K ⁻¹]	$v_{sp,0}^*$ [cm ³ g ⁻¹]	E_{11}^0 [J mol ⁻¹]	S_{11}^0 [J mol ⁻¹ K ⁻¹]	s	V_{11}^0 [cm ³ mol ⁻¹]
Water	5336.5	-6.506	0.97034	-16,100	-14.7	0.861	0
PCL	5876 ± 50	3.824 ± 0.01	0.8873 ± 0.005	-	-	0.818	-

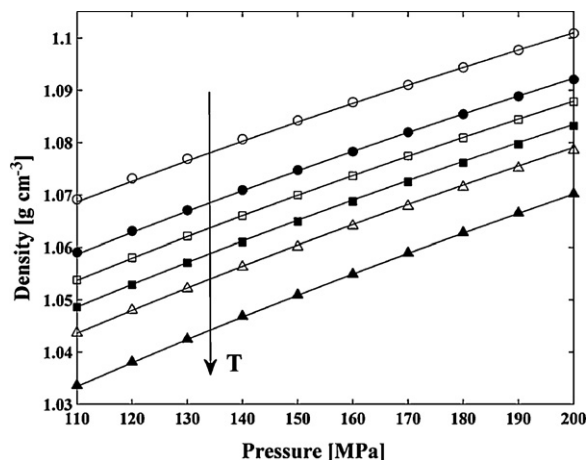


Fig. 7. Fitting of PVT data for PCL by using NRHB model. The arrow indicates the increasing direction of temperature. Marker symbols for data determined at six temperatures are, respectively, 400 K (○), 421 K (●), 431 K (□), 441 K (■), 451 K (△) and 471 K (▲). The lines represent the theoretical results. Fitting parameters are reported in Table 4.

cross-H bonds, related to the limited amount of proton acceptor groups available for the interactions (the concentration of ester linkages amounts to around 0.0088 mol g⁻¹ of polymer). The model predicts (results not shown) that the number of cross-HB decreases with temperature as is expected in view of the exothermicity of the process. Again, predictions obtained imposing $V_{11}^0 = 0$ are quantitatively and qualitatively close to those obtained for the case $V_{11}^0 \neq 0$.

Qualitatively analogous results are obtained also in the case of one proton acceptor group per repeating unit of PCL.

These outcomes of the theoretical analysis could be used to check the reliability of the whole modelling approach by comparison with experimental results obtainable from FTIR spectroscopy. In fact, specific in situ FTIR transmission experiments have been planned on PCL films exposed to water vapour at different relative pressures and temperatures, to gather quantitative information on the amount of different types of HB interactions established between sorbed water molecules and between sorbed water molecules and proton acceptor groups on polymer backbone.

4.3. Interpretation of sorption isotherms using NRHB model

Despite its more complex structure, the NRHB model still maintains the same total number of fitting parameters as for PS. Three lattice fluid scaling parameters, i.e. ε_h^* , ε_s^* and $v_{sp,0}^*$, are used to describe the PVT behaviour of pure PCL and have been determined by fitting PVT data. A numerical procedure analogous to that used for PS has been followed. In Fig. 7 results of model fitting are plotted

Table 5
NRHB mean field interaction parameter and cross-HB parameters for the PCL–water system, as obtained from data fitting of experimental sorption isotherms.

Proton acceptor per PCL repeating unit	k_{12}	E_{12}^0 [J mol ⁻¹]	S_{12}^0 [J mol ⁻¹ K ⁻¹]	V_{12}^0 [cm ³ mol ⁻¹]
1	-0.1152 ± 0.005	-11,130 ± 200	-6.13 ± 0.1	0
2	-0.0922 ± 0.005	-11,270 ± 200	-11.59 ± 0.1	0

along with experimental data and the corresponding values for parameters are reported in Table 4. As for the case of PS, the values of s_i , evaluated using UNIFAC calculation procedure, have been taken from the literature [31]. Again, three lattice fluid parameters and two hydrogen bonding parameters (i.e. internal energy, and entropy of formation of hydrogen bonds, E_{11}^0 and S_{11}^0) have been used for pure water. Their values have been taken from the literature [41] and are reported in Table 4 as well.

Interpretation of water sorption isotherms using NRHB has been then performed by using three fitting parameters: the water–PCL mean field interaction parameter, k_{12} , and the internal energy and the entropy of formation of water–PCL hydrogen bonds, i.e. E_{12}^0 and S_{12}^0 (best fitting values are reported in Table 5 along with the 95% confidence intervals).

As already mentioned, the volume of formation of self- and cross-HB has been taken to be equal to zero. In analogy to the case of PS, two different cases have been considered, differing in the number of proton acceptor groups per polymer repeating unit, i.e. one and two proton acceptor groups per repeating unit of PCL. Moreover, the values of energy and entropy of formation of self-HB between water molecules sorbed into PCL are assumed to take the same values as for the case of pure water. As for the case of PS model, best-fitting values of E_{12}^0 are close to each other in the case of one and two proton acceptor groups per repeating unit of polymer, while values of S_{12}^0 are quite different.

As an example, fitting of sorption isotherms using NRHB model with two proton acceptor groups per repeating unit of PCL, is reported in Fig. 8. A statistical analysis of the parameters has been carried out, similar to that performed for the case of PS model. In Fig. 8 are in fact reported also bounds, for the case of 310 K isotherm, obtained by perturbing the estimated fitting parameters within the confidence intervals. Again, the analysis indicates that the reliability of the set of estimated parameters is satisfactory. The same quality of fitting is attained also in the case of NRHB model with one proton acceptor group.

Finally, in Fig. 9 are reported the values of n_{11}^{wp}/m_2^{am} and n_{12}^{wp}/m_2^{am} as a function of water mass fraction in the amorphous phase of PCL, as predicted by using NRHB model with two proton acceptor groups per repeating unit of PCL at 298 and 310 K. Qualitatively similar results are obtained in the case of one proton acceptor group per repeating unit of PCL. The shape of the curves as well as the trend with temperature are similar to the predictions of PS model.

By comparing the results of PS and NRHB models in interpreting the experimental sorption isotherms, it is evident that the two approaches exhibit very similar qualitative and quantitative behaviours. Also the numerical values predicted for n_{11}^{wp}/m_2^{am} and n_{12}^{wp}/m_2 using NRHB model are very close to those obtained applying PS approach. Quantitative differences have been found only for the entropic cross-HB parameter, the absolute values of S_{12}^0 evaluated using the NRHB approach being significantly lower.

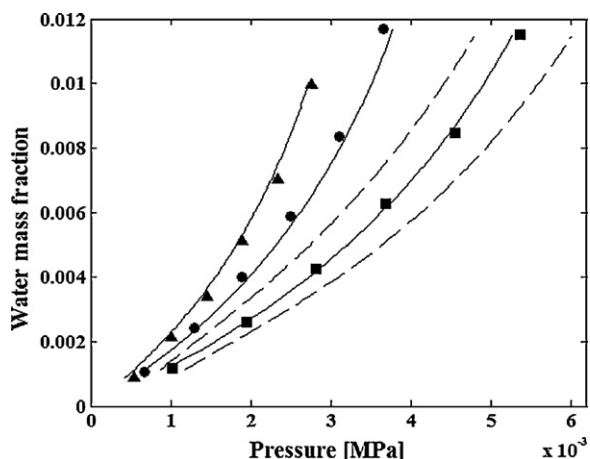


Fig. 8. Fitting of water sorption isotherms in PCL by using NRHB model. The case of two proton acceptor groups per repeating unit of PCL is reported. Model fitting is represented by continuous lines. Water mass fraction is referred to the amorphous phase of PCL. Marker symbols for data obtained at three temperatures are, respectively, 298 K (\blacktriangle), 303 K (\bullet) and 310 K (\blacksquare). Fitting parameters are reported in Table 5. Dashed lines represent statistical bounds for predicted 310 K isotherm.

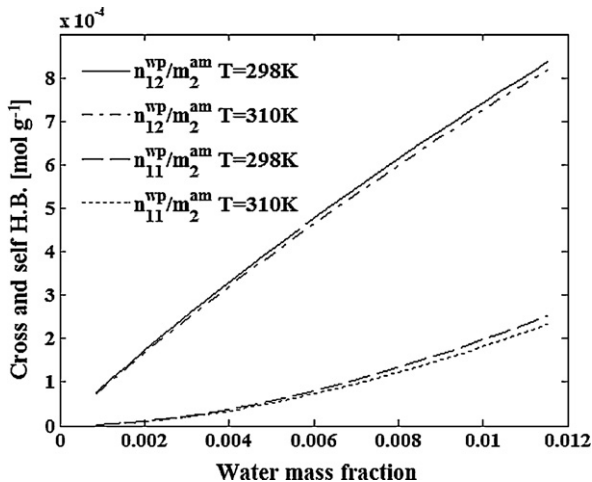


Fig. 9. Predicted values of water self-HB and water–polymer cross-HB. In terms of moles of established hydrogen bonds, in the PCL–water mixture, per gram of dry amorphous polymer as a function of water mass fraction; predictions performed by using NRHB for the case of two proton acceptor groups per repeating unit of PCL at $T=298$ and 310 K. Water mass fraction is referred to amorphous phase of PCL.

5. Concluding remarks

A satisfactory quality of fitting of equilibrium sorption isotherms of water in amorphous regions of PCL can be obtained with lattice fluid thermodynamic models only by accounting for the formation of self- and cross-HB. In fact, both PS and NRHB models display a better fitting capability of water vapour sorption isotherms in amorphous PCL as compared to LF model.

Overall, PS and NRHB theories exhibit a similar qualitative and quantitative behaviour, differing significantly only for the cross-HB entropic parameter. Regarding PS approach, the two cases examined, one assuming $V_{11}^0 = 0$ and the other $V_{11}^0 \neq 0$, both display a very close behaviour in terms of fitting of sorption isotherm, of prediction of hydrogen bond formation and of values of relevant parameters. Only the value of the HB entropic parameter differs appreciably.

The assessment of appropriateness of the hypotheses adopted in using these approaches for the description of water sorption thermodynamics in PCL, with particular reference to HB interactions

issue, is certainly not feasible on the basis of the sole gravimetric data. A more exhaustive analysis can be performed if supported by experimental data for the amount and strength of HB interactions [41]. To this aim, a valuable help could be provided by FTIR in situ spectroscopy. In fact, spectroscopic analysis performed on PCL–water mixtures could be used to determine experimental values for energy and entropy of formation of cross-HB and to gather qualitative and quantitative information on the amount and type of self- and cross-HB forming in the mixture.

List of symbols

a_j^1	number of proton acceptor groups of kind j present on a molecule of type 1
d_i^1	number of proton donor of type i on the molecule of type 1
E_{ij}^0	molar internal energy of formation of hydrogen bonding between proton donor group of type i and proton acceptor group of type j [J mol^{-1}]
G_{ij}^0	molar Gibbs energy of formation of hydrogen bonding between proton donor group of type i and proton acceptor group of type j [J mol^{-1}]
k_{12}	mean field lattice fluid binary interactional parameter
l_i	parameter defined in Ref. [34]
m	number of types of proton donors
m_1	mass of water [g]
m_2^{am}	mass of amorphous phase of PCL [g]
m_2^{cry}	mass of crystalline phase of PCL [g]
$M.W.$	molecular weight [g mol^{-1}]
n	number of types of proton acceptors
n_{11}^{wp}	moles of self-hydrogen bondings between the proton donor and the proton acceptor groups of water molecules within the polymer–water mixture [mol]
n_{12}^{wp}	moles of cross-hydrogen bondings between the proton donor groups of the water molecules and the proton acceptor groups of the PCL within the polymer–water mixture [mol]
N	number of molecules in the lattice
N_r	number of lattice sites
N_0	number of empty sites in the lattice
N_{ij}	number of hydrogen bondings involving a proton donor of type i and a proton acceptor of type j
N_{11}^{V}	number of water self-hydrogen bondings between the proton donor and the proton acceptor groups of water molecules within water vapour phase.
N_{11}^{wp}	number of self-hydrogen bondings between the proton donor and the proton acceptor groups of water molecules within the polymer–water mixture
N_{12}^{wp}	number of cross-hydrogen bondings between the proton donor groups of the water molecules and the proton acceptor groups of the PCL, within the polymer–water mixture
P	pressure of the system [MPa]
P^*	characteristic pressure of pure components or average characteristic pressure for the mixture [MPa]
P_1^*	characteristic pressure of component 1 [MPa]
P_2^*	characteristic pressure of component 2 [MPa]
\tilde{P}_1	scaled pressure of pure component 1
q	average number of lattice contacts per molecule in the PCL–water mixture
q_1	number of lattice contacts per molecule for component 1
r	average number of lattice cells occupied by one molecule in the PCL–water mixture

r_i	number of lattice cells occupied by one molecule of component i	ε_h^*	enthalpic contribution to lattice fluid interaction energy per mole of segment [J mol^{-1}]
r_1	number of lattice cells occupied by one molecule of component 1	ε_{h1}^*	enthalpic contribution to lattice fluid interaction energy per mole of segment of component 1 [J mol^{-1}]
r_2	number of lattice cells occupied by one molecule of component 2	ε_{h2}^*	enthalpic contribution to lattice fluid interaction energy per mole of segment of component 2 [J mol^{-1}]
R	universal gas constant [$\text{J K}^{-1} \text{mol}^{-1}$]	ε_s^*	entropic contribution to lattice fluid interaction energy per mole of segment [$\text{J mol}^{-1} \text{K}^{-1}$]
s	number of lattice contacts per segment of molecule	ε_{s1}^*	entropic contribution to lattice fluid interaction energy per mole of segment of component 1 [$\text{J mol}^{-1} \text{K}^{-1}$]
s_1	number of lattice contacts per segment of molecule of component 1	ε_{s2}^*	entropic contribution to lattice fluid interaction energy per mole of segment of component 2 [$\text{J mol}^{-1} \text{K}^{-1}$]
s_2	number of lattice contacts per segment of molecule of component 2	ε_{ii}^*	average lattice fluid interaction energy per mole of segment of one molecule of component i [J mol^{-1}]
s_i	number of lattice contacts per segment of molecule of component i	ε_{ij}^*	average lattice fluid interaction energy per mole of average segment in the binary i – j mixture [J mol^{-1}]
S_{ij}^0	molar entropy of formation of hydrogen bonding between proton donor group of type i and proton acceptor group of type j [$\text{J mol}^{-1} \text{K}^{-1}$]	θ_i	surface fraction of component i
T	temperature of the system [K]	$\mu_{1,LF}$	lattice fluid contribution to the chemical potential of water [J mol^{-1}]
T^*	characteristic temperature of pure components or average characteristic temperature for the mixture [K]	$\mu_{1,H}$	hydrogen bonding contribution to the chemical potential of water [J mol^{-1}]
T_1^*	characteristic temperature of component 1 [K]	μ_1	chemical potential of water [J mol^{-1}]
T_2^*	characteristic temperature of component 2 [K]	ν_H	average number of hydrogen bonds per molecular segment
\tilde{T}_1	scaled temperature of pure component 1	ν_d^i	average number of proton donor of type i per molecular segment
ν^*	close-packed volume of an elementary cell of the lattice [$\text{cm}^3 \text{mol}^{-1}$]	ν_{i0}	average number of unbonded proton donor of type i per molecular segment
$\tilde{\nu}$	scaled lattice fluid volume of the pure components or of the mixture (i.e. $V_{LF}/rN\nu^*$)	ν_a^j	average number of proton acceptor of type j per molecular segment
ν_{sp}^*	close packed specific volume of the pure components [$\text{cm}^3 \text{g}^{-1}$]	ν_{0j}	average number of unbonded proton acceptor of type j per molecular segment
$\nu_{sp,0}^*$	temperature independent contribution to close packed specific volume of the pure components [$\text{cm}^3 \text{g}^{-1}$]	ν_{ij}	average number per molecular segment of hydrogen bonding established between a proton donor of type i and a proton acceptor of type j
$\nu_{sp,01}^*$	temperature independent contribution to close packed specific volume of the pure component of type 1 [$\text{cm}^3 \text{g}^{-1}$]	ρ^*	close packed density of the pure components or of the mixture [g cm^{-3}]
$\nu_{sp,02}^*$	temperature independent contribution to close packed specific volume of the pure component of type 2 [$\text{cm}^3 \text{g}^{-1}$]	ρ_{LF}	lattice fluid contribution to the system density [g cm^{-3}]
$\nu_{sp,1}^*$	characteristic parameter for a given homologous series [$\text{cm}^3 \text{g}^{-1} \text{K}^{-1}$]	$\bar{\rho}$	scaled density of pure components or of the mixture
V	volume of the polymer–penetrant mixture [cm^3]	ρ_1^*	close packed density of component 1 [g cm^{-3}]
V_{LF}	lattice fluid contribution to volume of the polymer–penetrant mixture [cm^3]	ρ_2^*	close packed density of component 2 [g cm^{-3}]
V_{ij}^0	molar change of volume associated to the formation of hydrogen bonding between proton donor group of type i and proton acceptor group of type j [$\text{cm}^3 \text{mol}^{-1}$]	ϕ_1	'close packed' volumetric fraction of component 1
w^{am}	mass fraction of amorphous phase in the pure PCL	ϕ_2	'close packed' volumetric fraction of component 2
w_1^{tot}	ratio of mass of water to total mass of system	ϕ_1^{am}	'close packed' volumetric fraction of water referred only to the amorphous phase of PCL
w_1^{am}	ratio of mass of water to the sum of mass of sorbed water and mass of amorphous part of PCL	χ_C	percent by weight crystallinity of PCL
X_{12}	scaled lattice fluid energy of mixing for binary mixtures	ω_1	number of configurations available to a molecule of component 1 in the close-packed state
z	lattice coordination number		

Greek letters

ΔH_m	melting enthalpy of semicrystalline PCL [J g^{-1}]
ΔH_m^0	melting enthalpy of 100% crystalline PCL [J g^{-1}]
Γ_{00}	non-random factor for the distribution of an empty site around another empty site in the lattice
Γ_{11}	non-random factor for the distribution of a site occupied by component 1 around another site occupied by component 1 in the lattice
ε_{ii}	lattice fluid interaction energy per mole of contact i – i [J mol^{-1}]
ε^*	average lattice fluid intersegmental interaction energy per mole of average segment in the polymer–water mixture [J mol^{-1}]

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