

# A comparison of three first principles methods for predicting solute–polymer affinity, and the simultaneous biodegradation of phenol and butyl acetate in a two-phase partitioning bioreactor

Eduardo E. Poleo and Andrew J. Daugulis\*

## Abstract

**BACKGROUND:** Solid–liquid two-phase partitioning bioreactors (TPPBs) use polymers as the sequestering phase to reduce the concentration of substrates to sub-inhibitory levels and enhance biodegradation performance. Polymer selection for TPPBs is challenging due to the almost infinite variety of target substrates to be degraded, and the variability and complexity of polymer composition and structure.

**RESULTS:** Three different polymer selection criteria, based on either solubility parameters or activity coefficients, were assessed via experimental partitioning coefficients (PCs) for phenol and butyl acetate, two substantially different target contaminant molecules, and the relative ability of the three methods to predict effective polymers was assessed. The best method was also applied to predict which waste polymers would be effective for sequestering these molecules, and TPPB degradation tests were conducted to confirm the effectiveness of a single identified polymer and selected waste polymers.

**CONCLUSION:** An effective polymer selection criterion was identified and the identified polymer showed a high capacity to absorb both phenol and butyl acetate. Both substrates were successfully degraded in solid–liquid TPPBs using the selected polymer and using mixtures of waste polymers.

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**Keywords:** biodegradation; polymer selection; TPPB; solubility parameter; polymer thermodynamics

## INTRODUCTION

Two-phase partitioning bioreactors (TPPBs) utilize a non-aqueous phase that acts as a reservoir for high concentrations of inhibitory substrates. This sequestering phase reduces the aqueous substrate concentration to sub-cytotoxic levels, and progressively re-releases it to the cell-containing aqueous phase in order to respond to the microbial metabolic demand. This dynamic process is regulated by thermodynamic equilibrium (the relative affinity of the substrate between the aqueous and sequestering phases) and cell metabolism.<sup>1</sup>

Although immiscible organic solvents were originally used as the partitioning phase in TPPBs it has been shown that polymer-based systems can match and even outperform their liquid–liquid counterparts in many different types of applications.<sup>2–4</sup> In light of this superior performance by polymer-based TPPBs, it is extremely important to make the distinction between two types of polymers, and their respective modes of cell or solute interaction. Synthetic polymeric materials, usually called ‘resins’, consist of rigid, macroporous beads that are often highly cross-linked and are engineered to possess very high specific surface areas. The mechanism by which these glassy, styrene-divinylbenzene-based resins function is via surface interactions, that is, by adsorption.

The use of such resins for cell adsorption (immobilization) has a long history,<sup>5,6</sup> and these hard, crystalline resins have also been used for the adsorption of target molecules for the *in situ* removal of inhibitory fermentation products,<sup>7–9</sup> as has recently been reviewed.<sup>10</sup>

In contrast to such adsorptive polymers, our work using polymers to replace organic solvents in TPPBs utilizes polymers with segmented block architecture, containing soft, amorphous segments which allow solute absorption and permeation within the bulk polymer mass itself, akin to the dissolution of a solute into a liquid organic phase. That is, the uptake of target molecules by our amorphous thermoplastic polymers is by absorption, not adsorption, as has been clearly demonstrated.<sup>11</sup> Such absorptive polymers have formed the basis of the important area of controlled drug delivery, a scientific and technological field that has been

\* Correspondence to: Andrew J. Daugulis, Department of Chemical Engineering, Dupuis Hall, 19 Division St. Queen's University, Kingston, Ontario, Canada K7L3N6. Email: andrew.daugulis@chee.queensu.ca

Department of Chemical Engineering, Dupuis Hall, 19 Division St. Queen's University, Kingston, Ontario, Canada K7L3N6

studied for more than 30 years.<sup>12</sup> Surface area is immaterial for solute sorption in such cases and indeed, our polymers are smooth, showing no propensity for cell attachment.<sup>13</sup> Given that absorption is based on functional group interactions, it is not surprising that polymers of the kind that we use, in contrast to, for example, ion exchange resins, have little or no attraction for ionic species or salts, such as are typically found in fermentation media. Also significant is the fact that our soft, amorphous polymers, which are used as-received from suppliers, are significantly less expensive<sup>14,15</sup> (c. \$5–6 per kg) than most highly engineered high-surface area resins<sup>16</sup> (\$90–200 per kg). Polymers are in virtually all cases biocompatible, non-bioavailable and easy to handle, and perhaps most importantly, polymers possess a large variety of different chemical structures that can be combined into chemical mixtures as blends of individual monomers or as co-polymers, allowing a wider range of solute affinities.<sup>17</sup> Nevertheless, despite their versatility, the complex structure of polymers makes solute–polymer interactions difficult to predict, and as a consequence rational selection of polymers for specific TPPBs applications is challenging, certainly more so than predicting solvent–solute interactions, which have been well described by classical thermodynamic methods.<sup>18</sup>

In a previous study we showed that it is possible to find two polymers to target two distinct substrates, phenol and butyl acetate, whose chemical and physical properties differ considerably.<sup>19</sup> Phenol is a relatively polar and toxic aromatic compound possessing moderate aqueous solubility, low volatility, and high capacity for hydrogen bonding; butyl acetate is a considerably more hydrophobic and less toxic linear molecule, with lower aqueous solubility and high volatility. The selected polymers were identified by trial-and-error screening of a number of polymers available in our group but, although TPPB tests were highly effective, such random polymer testing does not provide a basis for polymer selection for other TPPB applications.

In an attempt to generate a more rational approach for polymer identification, properties such as the polymer hardness, solute octanol–water partitioning coefficient ( $\log K_{O/W}$ ) and polymer crystallinity, have previously been considered to try to explain polymer–solute absorption,<sup>20</sup> although it has been shown that such parameters are inadequate when attempting to describe or predict all possible polymer–solute interactions.<sup>21</sup> Recently, a first principles' approach for polymer selection for TPPBs was proposed<sup>21</sup> in which polymer absorption of highly hydrophobic solutes (polyaromatic hydrocarbons) was initially described in terms of polymer accessibility, which was correlated with the degree of crystallinity and the glass transition temperature of the polymer ( $T_g$ ). Additionally, specific polymer–solute thermodynamic affinity was characterized using the overall Hildebrand solubility parameter method. Hildebrand solubility parameters (SPs) were originally intended for non-polar non-electrolyte systems<sup>22</sup> and are commonly used to describe polymer–solute binary interactions in several industrial applications (e.g. protective coatings) due to their widespread availability and simplicity.<sup>23</sup> However, solid–liquid TPPBs are complex three component systems (polymer–solute–water), which can provide a wide range of possible interactions. Moreover, the Hildebrand solubility parameter approach can account only for the polymer–solute interactions, completely neglecting the presences of water and its corresponding effects.

The current work has provided an extension of the above polymer selection criterion: three different methods used to characterize polymer–solute interactions were compared,

Hildebrand SPs, Hansen solubility parameters (HSPs) and activity coefficient predictions. Such methods, to the best of our knowledge, are the only thermodynamic approaches available to describe polymer–solute interactions.<sup>21,24</sup> The methods were tested against two TPPB substrates, phenol and butyl acetate whose chemical and physical properties, as noted, differ considerably<sup>19</sup> thereby providing a good test of the three predictive methods. The methods were used to identify a single polymer with affinity for both target molecules that could operate effectively in a TPPB, and also to identify waste polymers for the same purpose. TPPB biodegradation experiments were then undertaken to demonstrate the subsequent performance of the identified polymers.

## EXPERIMENTAL

### Materials

All medium components and powder-free nitrile rubber examination gloves were purchased from Fisher Scientific (Guelph, Canada). High density polyethylene, phenol (99%) and butyl acetate (>99%) were obtained from Sigma–Aldrich. The various grades of Pebax<sup>®</sup> were purchased from Arkema (Burlington, Ontario, Canada), Hytrel<sup>®</sup> 3548 was supplied by DuPont (Kingston, Ontario, Canada), polyisoprene and nitrile butadiene rubber (21% acrylonitrile content) were purchased from Scientific Polymer (Ontario, New York, USA), neoprene and nitrile rubber tubing were obtained from Rubber Sheet Roll Inc. (Shippensburg, Pennsylvania, US), nitrile rubber O-rings and polypropylene tubing were purchased from Cole-Parmer (Montreal, Quebec, Canada), and nitrile O-rings were purchased from Levac Supplied Limited (Kingston, Ontario, Canada). Used tire rubber was obtained from Recovery Technologies Canada Inc. (Cambridge Ontario) in the form of rubber 'crumble'. Crumble is obtained by a cryogenic process in which tires are cooled to a temperature lower than  $-80^\circ\text{C}$ . Below this glass transition temperature rubber becomes brittle, and size reduction can be accomplished by crushing and grinding, after which steel and fibre separation is easily accomplished. The crumble is claimed to have an unaltered chemical composition relative to the original tires, and is currently used for rubber modified asphalt, moulded rubber products and sports surfaces.<sup>25</sup>

### Organisms and growth medium

A microbial consortium to degrade phenol and butyl acetate was obtained via selective enrichment, as previously described.<sup>19</sup> The growth medium consisted of  $2\text{ g L}^{-1}$   $(\text{NH}_4)_2\text{SO}_4$ ,  $0.75\text{ g L}^{-1}$   $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $2\text{ g L}^{-1}$   $\text{K}_2\text{HPO}_4$ ,  $2\text{ g L}^{-1}$   $\text{KH}_2\text{PO}_4$ ,  $0.1\text{ g L}^{-1}$  yeast extract,  $1\text{ mL L}^{-1}$  trace element solution, prepared in tap water as previously described.<sup>26</sup> Various concentrations of phenol and/or butyl acetate as carbon sources were employed depending on the experiment.

### Partitioning coefficient measurements

All partitioning coefficient (PC) experiments were performed in quadruplicate with four different polymer masses, ranging from 1 to 4 g. The desired polymer mass was placed in 20 mL scintillation vials, following the addition of 18 mL of a solution containing known concentrations of both butyl acetate and phenol dissolved in Milli-Q water. The vials were sealed and shaken at  $30^\circ\text{C}$  and 180 rpm overnight to ensure equilibrium. Final aqueous concentrations were measured and the PC values were obtained through mass balances.

### Solid–liquid biodegradation tests

TPPB biodegradation tests were undertaken in a sequencing batch mode as previously described<sup>19</sup> using 2.7 L of medium in a sterile 5 L New Brunswick Scientific BioFlo III with 500 or 1000 mg L<sup>-1</sup> of phenol and butyl acetate, followed by inoculation. Operation in TPPB mode utilized a single polymer (150 g of Pebax® 2533 corresponding to a polymer fraction of 5%) or waste polymer mixtures (75 g of rubber tire and 250 g of nitrile rubber, corresponding to a total polymer fraction of 10.8%). The pH and temperature were controlled at 6.9 and 30°C, respectively, and agitation and aeration were maintained at 400 rpm and 1 L min<sup>-1</sup> unless the dissolved oxygen (DO) percentage decreased to a value less than 40%, in which case both were increased to 500 rpm and 4 L min<sup>-1</sup>. At the end of each cycle 80% of the reaction broth was pumped out and replaced with fresh medium and substrate to start a new cycle. Each cycle proceeded with the inoculum obtained from the previous cycle except for the initial cycle whose inoculum was prepared separately in shake flasks. A typical cycle lasted 22 h divided as follows: fill phase 1 min, reaction phase approximately 10 h, idle phase 12 h, decant phase 5 min.

### Analytical procedures

Phenol, butyl acetate and cell concentrations were determined as described previously.<sup>19</sup>

## RESULTS AND DISCUSSION

### Polymer selection

In early research involving solid–liquid TPPBs polymer absorption capacity was explained in somewhat qualitative terms based on general information available, and the possible interactions that may be occurring between the polymer and target molecule,<sup>17,20</sup> such as polarity, hydrogen bonding potential, and polymer hardness, among others. Recently a more rational approach has been proposed using simple first principles considerations to better understand the structural and chemical interactions that govern polymer absorption in the context of TPPBs. As a result, polymer absorption has been characterized by means of two main factors: polymer accessibility and thermodynamic affinity.<sup>21</sup>

Polymer accessibility is determined primarily by the degree of crystallinity and the glass transition temperature of the polymer. In the case of block copolymers and partially crystalline homopolymers high degrees of crystallinity generally translate into poor uptake capacities simply because the crystalline domain is unable to participate in absorption due to its greater rigidity and resistance to solute penetration. This high degree of rigidity is what substantially precludes adsorptive resins from allowing permeation of solutes into the polymer matrix. In addition, if the amorphous segment of these polymers possesses glass transition temperatures ( $T_g$ ) greater than the operating temperatures, the polymer will lack significant chain and segmental mobility to allow the diffusion of even small molecules at such operating conditions. Thus, effective block copolymers and homopolymers must possess just enough crystalline domains to provide acceptable mechanical properties (i.e. they make the polymer solid), and a larger amorphous phase capable of participating in the absorption process. Additionally, the amorphous phase must have a considerable lower  $T_g$  than the operating temperature to ensure enough segmental and chain motion.<sup>21</sup>

In contrast to block copolymers, random copolymers possess a non-regular distribution of the monomers along their structure preventing the formation of clearly defined soft and hard segments.<sup>27</sup> Owing to this structural irregularity crystallization is more difficult in random copolymers and in addition they tend to present intermediate properties to the corresponding homopolymers.<sup>28</sup>

The polymers used in this work were initially selected using the accessibility criteria described above. As seen in Table 1 all of the polymers selected, except for HDPE, possessed relatively small amounts of a hard crystalline phase. Polymers shown in Table 1 also had  $T_g$  values considerably lower than the operating temperature of the experiments (30°C). In the case of styrene butadiene rubber and nitrile butadiene rubber, which are random copolymers, it is suspected that these polymers do not possess multiple structural domains as opposed to the other commercial block copolymers studied, and for the purpose of this work they are considered completely amorphous with structural and thermodynamic contributions arising from all of their constituents.<sup>28</sup>

The accessibility criteria are an initial guideline to predict whether a given polymer has the structural characteristics to provide general solute absorption, nevertheless such criteria say little about the specific polymer–solute interactions that confer solute–polymer affinity. In order to effectively select polymers for a given TPPB application the thermodynamic affinity between candidate polymers and target molecules must be assessed. Polymer solute interactions can be characterized by using the three thermodynamic tools available: Hildebrand SPs, Hansen solubility parameters (HSPs), and activity coefficient methods.<sup>23,29,30</sup> In the current work the performance of each method was assessed using the normalized PCs for butyl acetate and phenol presented in Table 2. The normalized PCs were obtained by dividing the experimentally-determined PCs by their corresponding amorphous polymer fraction; thus the normalized PCs account only for the mass of polymer which was actively participating in the absorption process, that is, which has an affinity for the solute.

### Hildebrand solubility parameter

The first approach using solubility parameters was developed by Hildebrand and Scot,<sup>22</sup> and they defined solubility parameters (SPs) as shown in Equation (1):

$$\delta = \sqrt{\frac{\Delta H_v}{V}} \quad (1)$$

where  $\Delta H_v$  is the heat of vaporization and  $V$  corresponds to the molar volume of the given molecule.

The SPs represent a measure of the cohesive energy density and provide a quantitative estimate of the potential interaction between materials;<sup>23</sup> according to traditional polymer solution theory smaller differences in SPs minimize the activity of a solute in a given polymer. This ultimately translates into greater uptake capacities, and therefore the smaller the differences in SPs between polymer–solute pairs the higher the expected partitioning coefficient.<sup>21</sup>

Figure 1 shows the normalized PCs as a function of the differences in the corresponding Hildebrand SPs between polymers and solutes. Hildebrand solubility parameters for the polymers amorphous phase were obtained from the literature.<sup>31</sup> Ideally smaller solubility parameter differences should translate into higher partitioning coefficients, which would be seen as

**Table 1.** Relevant properties for commercial polymers

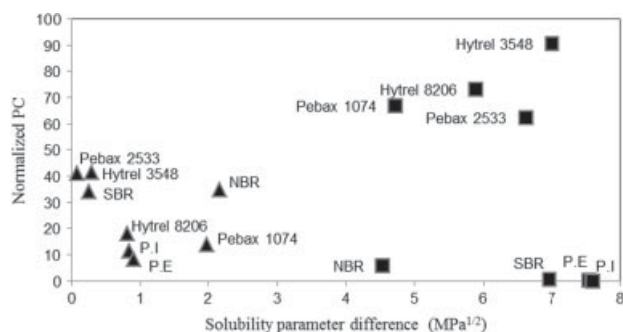
Polymer name	Structure arrangement	Active component	Fraction (%)	(T <sub>g</sub> , °C)
Hytrel <sup>®</sup> 8206	Block copolymer	Polyether	~ 50 <sup>a</sup>	-59
Hytrel <sup>®</sup> 3548	Block copolymer	Polyether	~ 50 <sup>b</sup>	-45
Pebax <sup>®</sup> 2533	Block copolymer	Polyether	80	-65
Pebax <sup>®</sup> 1074	Block copolymer	Polyether	55	-40
High density polyethylene (HDPE)	Homopolymer	Amorphous Polyethylene	≈ 25 <sup>c</sup>	≈ -124 <sup>d</sup>
Styrene-butadiene rubber (5% Styrene, SBR)	Random copolymer	Fully amorphous	100	≈ -76 <sup>d</sup>
Trans-Polyisoprene (P.I)	Homopolymer	Amorphous Polyisoprene	≈ 67 <sup>e</sup>	-68
Acrylonitrile/butadiene rubber (21% ACN, NBR)	Random copolymer	Fully amorphous	100	≈ -60 <sup>d</sup>

<sup>a</sup> Obtained from Ref. 17.  
<sup>b</sup> Assuming similar soft segment composition to 8206.  
<sup>c</sup> Obtained from values presented in Ref 36.  
<sup>d</sup> Obtained from values presented in Ref 37.  
<sup>e</sup> Obtained from values presented in Ref 38.

**Table 2.** PCs for different materials

Material	Butyl acetate PC		Phenol PC	
	Experimental	Normalized	Experimental	Normalized
Hytrel <sup>®</sup> 8206 <sup>a</sup>	9.2 ± 0.4	17.9 ± 0.7	37.4 ± 0.6	73.3 ± 1.1
Hytrel <sup>®</sup> 3548	22.9 ± 0.7	41.6 ± 1.3	49.8 ± 0.9	90.5 ± 1.7
Pebax <sup>®</sup> 2533	32.7 ± 3.6	40.9 ± 4.5	50.0 ± 0.6	62.5 ± 0.8
Pebax <sup>®</sup> 1074	7.7 ± 1.4	13.9 ± 2.6	36.8 ± 0.9	66.8 ± 1.7
High density polyethylene	2.1 ± 0.03	8.4 ± 0.1	0 ± 0.07	0 ± 0.3
Styrene-butadiene rubber <sup>a</sup>	34.0 ± 1.8	34.0 ± 1.8	0.8 ± 0.3	0.8 ± 0.3
Trans-Polyisoprene	7.8 ± 0.3	11.6 ± 0.4	0.1 ± 0.06	0.2 ± 0.1
Acrylonitrile/butadiene rubber	34.8 ± 0.6	34.8 ± 0.6	6.0 ± 0.5	6.0 ± 0.5
Rubber tire	18.0 ± 1.5	—	1.2 ± 0.1	—
Nitrile rubber glove	26.6 ± 2.9	—	15.0 ± 1.0	—
Nitrile rubber tubing	20.2 ± 0.8	—	5.1 ± 0.2	—
Nitrile rubber O-ring (Levac Supplies Inc)	23.0 ± 1.8	—	7.3 ± 0.8	—
Nitrile rubber O-ring (Cole-Parmer)	11.7 ± 1.7	—	4.4 ± 0.9	—
Poly propylene tubing	18.5 ± 1	—	0.8 ± 0.05	—

<sup>a</sup> Data from Ref 19.

**Figure 1.** Hildebrand solubility parameter method assessment based on normalized PC and solubility parameter difference: ▲ butyl acetate, ■ phenol.

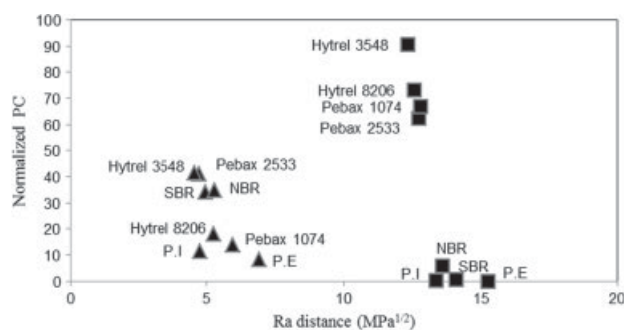
a plot with a curve sloping upward to the left. This trend is observable for butyl acetate, however, the trend is less clear for phenol as the data for phenol are considerably more scattered. In general, the solubility parameter difference between the polymers tested and phenol was greater than with butyl acetate. As will

be described later, this may be due to the higher polarity and hydrogen bonding character of phenol, which is not captured by the 'lumped' single solubility parameter as defined by Hildebrand and which therefore cannot be used to explain this observation given that Hildebrand SPs make no distinction between different types of interactions.

#### Hansen solubility parameter (HSP)

Hansen proposed an extension of the Hildebrand solubility parameters that could better capture the nature of the polar and hydrogen bonding interactions between materials.<sup>23</sup> In the HSP approach the solubility parameter is divided into three main contributions: atomic dispersion forces ( $\delta_D$ ), molecular dipole interactions ( $\delta_P$ ) and molecular hydrogen bonding ( $\delta_H$ ). Each contribution corresponds to a coordinate in the three dimensional 'Hansen Space'. The total solubility parameter for a substance can be calculated as the Euclidean norm of the vector arising from these three contributions, as shown in Equation (2):

$$\delta_{tot} = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2} \quad (2)$$



**Figure 2.** Hansen solubility parameter method assessment based on normalized PC and Ra values: ▲ butyl acetate, ■ phenol.

The relative HSP ‘distance’ between two different materials has been defined by Hansen and Skaarup<sup>23</sup> as

$$(Ra)^2 = 4 \cdot (\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2 \quad (3)$$

Similar to the Hildebrand approach, a smaller HSP distance (Ra) will translate into higher miscibility between materials and, again, a plot of PC vs Ra would result in a curve sloping upward to the left. HSPs for the polymer amorphous part were obtained from the HSPiP software v3.1. (Charles M. Hansen (<http://www.hansen-solubility.com>)). Figure 2 shows the relationship between the normalized partitioning coefficients and the HSP distance between the polymers and both solutes. In this case both solutes followed the expected trend showing higher PCs at smaller Ra distances. The only clear outlier was seen for polyisoprene for which the HSP method predicts a higher relative affinity compared with the other polymers; nonetheless significant improvement was found in the data for phenol compared with the Hildebrand method. This may be due to the fact that the HSP concept provides an explanation for the greater differences in solubility parameters observed between phenol and the studied polymers. As seen in Table 3 the hydroxyl group in phenol greatly enhances its polar and hydrogen bonding character, thus increasing the total HSP values. These solubility parameter values are considerably greater than those of most polymers, which usually possess long non-polar carbon chains. Polymer thermodynamic affinity to high SP solutes, such as phenol, could be potentially enhanced by the addition of polar or hydrogen bonding groups into the polymer structure, nevertheless the introduction of these groups reduces chain mobility and causes an increase in  $T_g$  which can be detrimental for polymer accessibility, as mentioned previously.<sup>21</sup>

#### Infinite dilution activity coefficient predictions

Activity coefficients can account for the non-idealities of a chemical substance in a mixture, and can be defined as shown in

Equation (4):

$$\gamma_i \equiv \frac{a_i}{x_i} \quad (4)$$

where  $\gamma_i$  is the activity coefficient of the substance  $i$ ,  $a_i$  corresponds to the activity of the substance  $i$  in the mixture and  $x_i$  is the molar fraction of the compound in the mixture.<sup>32</sup> As the molar fraction of the compound approaches zero the activity coefficient reaches a defined fixed value that can be expressed by the following limit equation:<sup>33</sup>

$$\gamma_{i,x \rightarrow 0} = \lim_{x \rightarrow 0} (\gamma_i) \quad (5)$$

For solid–liquid TPPB systems if infinite dilutions conditions are met, the corresponding PC can be estimated as the ratio of the independently determined infinite dilution activity coefficients, as shown in Equation (6):

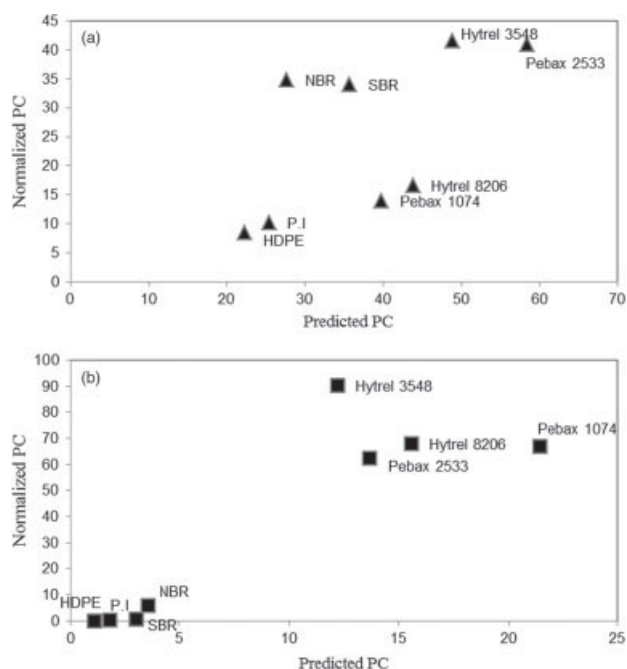
$$PC = \frac{\gamma_{solute,x \rightarrow 0}^{aq}}{\gamma_{solute,x \rightarrow 0}^{polymer}} = \frac{\Omega_{solute,x \rightarrow 0}^{aq}}{\Omega_{solute,x \rightarrow 0}^{polymer}} \quad (6)$$

where  $\gamma_{solute,x \rightarrow 0}^{aq}$  is the molar based infinite dilution activity coefficient of the target solute in the aqueous phase,  $\gamma_{solute,x \rightarrow 0}^{polymer}$  corresponds to the molar based infinite dilution activity coefficient of the target solute in the polymer phase. The  $\Omega$  coefficients are the equivalent mass basis activity coefficients. For the system studied infinite dilution conditions were assumed for the aqueous phase given that the maximum molar fraction of solute during the PC measurements was approximately  $4 \times 10^{-4}$ . Infinite dilution coefficients for butyl acetate and phenol in water were obtained from the literature.<sup>34</sup> For the polymer phase, infinite dilutions coefficients were estimated using a UNIFAC–vdW–FV model developed earlier,<sup>35</sup> which is a modified version of the original Oishi–Prausnitz model that allows predictions for polymer–aqueous systems. It was found that the activity coefficients for both phenol and butyl acetate in all polymers systems were constant (data not shown) throughout the range of concentration studied, suggesting that they also corresponded to infinite dilution activity coefficients.<sup>33</sup>

Figure 3 compares the UNIFAC predictions with the normalized PCs for butyl acetate and phenol, and in this case a perfect correlation would be a 45° straight line with the same axis values. The butyl acetate results show a coarse trend of this nature, although most of the predicted PCs are overestimated. On the other hand phenol predictions are more scattered and PC estimates are greatly underestimated. At best, the predictions obtained with the UNIFAC methods seem to be useful only for performing a relative assessment of the effectiveness of the polymers due to the great difference between the experimental and predicted PCs.

**Table 3.** Hansen solubility parameters for relevant compounds and materials

Compound/Polymer	Hansen solubility parameter (MPa <sup>1/2</sup> )				Ra distances (MPa <sup>1/2</sup> )	
	Dispersion	Polar	Hydrogen bonding	Overall	To butyl acetate	To phenol
Butyl acetate	15.8	3.7	6.3	17.4	—	—
Phenol	18.5	5.9	14.9	24.5	—	—
Styrene-butadiene	17.1	3.4	1.6	17.5	5.4	13.8
Nitrile rubber	16.7	5.8	1.8	17.8	5.3	13.6
Polypropylene	16.7	2.9	0.6	17.0	6.0	15.0



**Figure 3.** UNIFAC method assessment based on normalized PCs and predicted PCs: (a) butyl acetate, (b) phenol.

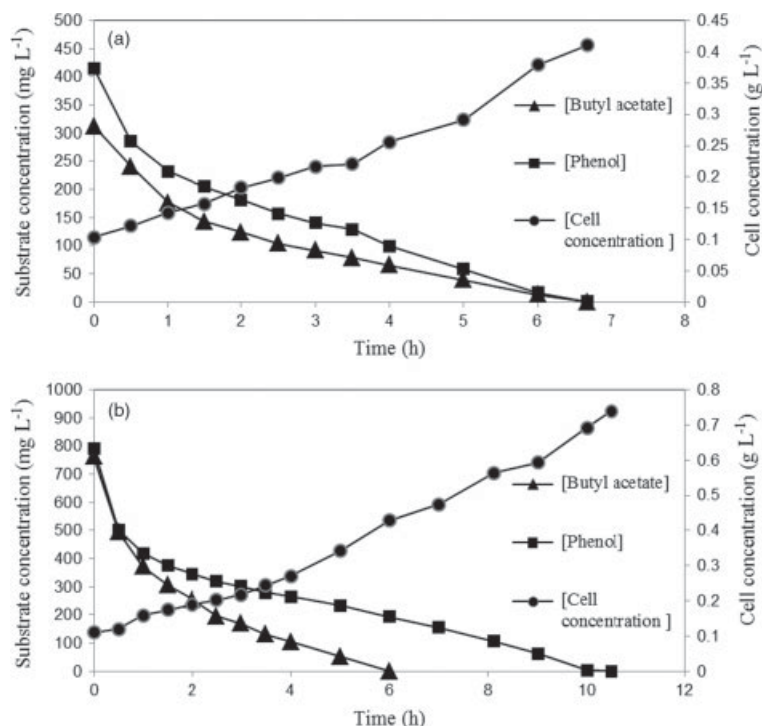
The solubility parameter methods, however, presented clear trends for the normalized PCs as a function of their corresponding SP differences/distance. In particular, the HSP method showed only slight scattering and gave a more direct insight into the relationship between the structure of the molecules and the interactions occurring in the system, proving to be superior to

its Hildebrand counterpart. The activity coefficient using the infinite dilution method showed the correct trends although the predictions obtained were considerably more scattered compared with the SP methods. Moreover, the PCs predicted differed greatly from the normalized values, making this method useful only for relative predictions, and the results may not justify the higher level of rigor employed in this case.

For the purposes of polymer selection, butadiene copolymers and Pebax<sup>®</sup> 2533 showed the highest experimental PCs for butyl acetate while all the polyether based copolymers showed relatively large PCs for phenol. Importantly, these polymers also had the smallest Ra using the HSP method, as seen in Fig. 2. Pebax<sup>®</sup> 2533 was therefore identified as the most suitable single polymer for both solutes studied due to the predicted high thermodynamic affinity (particularly seen in the HSP approach) and its high amorphous fraction, 80%, and low  $T_g$ . In our earlier work a mixture of Hytrel<sup>®</sup> 8206 and SBR was used for the simultaneous degradation of phenol and butyl acetate in a TPPB platform.<sup>19</sup> The selection of the single polymer Pebax<sup>®</sup> 2533 with increased uptake capacities (Table 2) through the HSP approach, represents a considerable practical improvement in that only a single target polymer needed to be used. To test the performance of Pebax<sup>®</sup> 2533, corresponding TPPB biodegradation experiments were carried out.

#### Solid–liquid TPPB using Pebax<sup>®</sup> 2355

Figure 4 shows the time course for the simultaneous biodegradation of phenol and butyl acetate using Pebax<sup>®</sup> 2355 at two different initial concentrations of 500 and 1000 mg L<sup>-1</sup>. The key performance metrics of the degradation of these substantially different substrates were related to the higher toxicity of phenol (and therefore the resulting phenol degradation rate), and the higher volatility of butyl acetate (and therefore the proportion of butyl acetate degraded vs volatilized). In the 500 mg L<sup>-1</sup> experiment



**Figure 4.** Compounds time course and cell concentration profile for the solid–liquid TPPB using Pebax<sup>®</sup> 2355. (a) Initial substrate concentration 500 mg L<sup>-1</sup>; (b) initial substrate concentration 1000 mg L<sup>-1</sup>.

**Table 4.** Performance parameters for solid–liquid TPPBs with Pebax<sup>®</sup> 2533, a mixture of rubber tire and NBR, a mixture of Hytrel<sup>®</sup> 8206 and SBR and a single phase system at different initial substrate concentrations

Performance for Pebax <sup>®</sup> 2533		
Performance parameter	500 mg L <sup>-1</sup>	1000 mg L <sup>-1</sup>
Total reaction time (h)	6.7	10.5
Phenol rate of degradation (mg L h <sup>-1</sup> )	75.0	95.2
Butyl acetate volatilized (%)	39.5	38.6
Butyl acetate degraded (%)	58.6	59.5
Performance for polymer mixture of rubber tire and NBR		
Total reaction time (h)	6.0	9.4
Phenol rate of degradation (mg L h <sup>-1</sup> )	83.3	106.7
Butyl acetate volatilized (%)	25.9	30.4
Butyl acetate degraded (%)	72.8	68.0
Performance for polymer mixture of Hytrel <sup>®</sup> 8206 and SBR <sup>a</sup>		
Total reaction time (h)	7.0	14.9
Phenol rate of degradation (mg L h <sup>-1</sup> )	71.4	66.8
Butyl acetate volatilized (%)	31.7	40.5
Butyl acetate degraded (%)	66.5	57.4
Performance for a single phase reactor <sup>a</sup>		
Total reaction time (h)	10.0	19.8
Phenol rate of degradation (mg L h <sup>-1</sup> )	50.7	46.4
Butyl acetate volatilized (%)	54.3	67.1
Butyl acetate degraded (%)	43.0	30.0

<sup>a</sup> Data from Ref 19.

the concentrations of both substrates decreased at the beginning of the reaction and, as has been demonstrated previously, such a decrease corresponds to polymer absorption in the case of phenol and the combined effect of volatilization, polymer absorption and degradation in the case of butyl acetate.<sup>19</sup> As a consequence the butyl acetate concentration profile always remained lower than that of phenol. The phenol concentration profile showed a sharp decrease after 3.5 h suggesting an increase in the phenol degradation rate. Both substrates were completely degraded after 6.7 h of reaction.

The 1000 mg L<sup>-1</sup> experiment also presented a sharp initial decrease in concentration, with butyl acetate disappearing more quickly and complete removal from the reactor after 6 h. The rate of phenol degradation increased considerably after butyl acetate's depletion until its complete degradation at 10 h. This trend is characteristic of a diauxic type of degradation as has been suggested before for this system.<sup>19</sup>

Table 4 shows the performance parameters of the biodegradation carried out at both initial concentrations. The enhanced performance of the Pebax<sup>®</sup> single polymer system was most apparent at the most challenging set of conditions (1000 mg L<sup>-1</sup> of each substrate), and showed a 40% improvement with respect to total reaction time and phenol degradation rate compared with our previous work using two distinct polymers. Relative to single-phase operation approximately 100% improvement was obtained by the Pebax<sup>®</sup> single polymer system for all performance metrics.

### Polymer selection for waste materials

To further test the capabilities of the HSP method, it was used to predict the relative effectiveness of rubber tire and common laboratory waste polymers to absorb phenol and butyl acetate, and therefore to potentially act as the sequestering phase in a TPPB. The predictions were carried out considering the following model waste polymers: SBR (tires), NBR (nitrile rubber gloves, tubing and O-rings) and polypropylene (tubing), which are commonly found in many industrial and research applications. Their PC values and their corresponding Ra values to phenol and butyl acetate are presented in Tables 2 and 3, respectively.

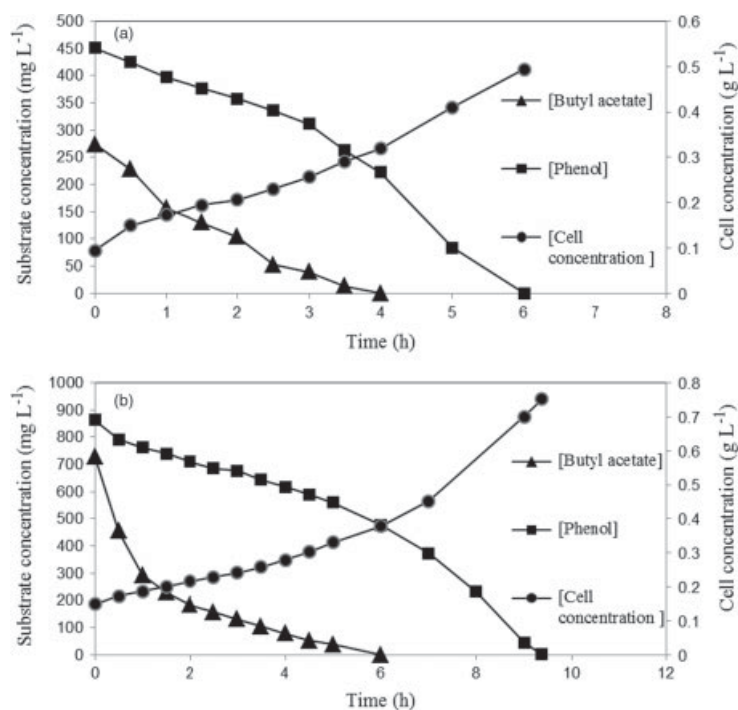
According to Table 3 nitrile rubber based materials would have the highest butyl acetate and phenol uptake capacities followed by SBR based materials. Lastly polypropylene materials were expected to have the smallest uptake capacities for both substrates. In terms of measured PC values, the NBR materials followed the expected trend having the highest affinity for both components, nevertheless polypropylene tubing showed a slightly higher PC for butyl acetate than did the rubber tires, contrary to what was expected. It is important to note that the exact composition of the materials tested is not provided for proprietary reasons, and therefore some of the PCs determined experimentally may be influenced by additives that are not considered in the predictions.

### Solid–liquid TPPB using a polymer mixture

TPPB experiments were conducted using a polymer mixture of rubber tire and NBR. The use of scrap tires in a TPPB system is appealing due to their significant global accumulation,<sup>25</sup> and scrap tires and their main constituent (styrene-butadiene rubber) have already been successfully employed in solid–liquid TPPBs applications.<sup>19,25</sup> Nevertheless, scrap tires have a negligible uptake affinity for phenol, thus NBR containing material had to be added to the mixture in order to ensure sub-inhibitory aqueous phenol concentrations. Pure NBR rubber was chosen as representative of these waste polymers in order for results not to be skewed by a particular supplier's formulation.

Figure 5 shows the phenol, butyl acetate and cell concentration time course at different initial substrate concentrations using a polymer mixture of rubber tire and NBR. A higher polymer mass fraction was employed this time to compensate for the lower phenol uptake capacity of nitrile rubber compared with other commercial polymers such as Pebax<sup>®</sup> 2533 and Hytrel<sup>®</sup> 8206. Figure 5(a) presents the biodegradation carried out at an initial concentration of 500 mg L<sup>-1</sup> for both substrates, and the concentration profile shows an initial decrease for both substrates due to polymer absorption, although the extent and rate of phenol sorption was not as pronounced as it was for the Pebax<sup>®</sup> single polymer system. Butyl acetate disappearance occurred after 4 h, followed by a sharp decrease in phenol concentration.

The degradation carried out at 1000 mg L<sup>-1</sup> showed a similar profile, with less extensive and less rapid phenol sorption, but with very rapid and complete butyl acetate disappearance. The relevant performance parameters for the removal of the two distinct substrates by the waste polymer mixture are shown in Table 4, and are comparable with the Pebax<sup>®</sup> single polymer system. These are encouraging results and demonstrate the capacity of waste polymers to also perform effectively in TPPBs, although at higher polymer fractions. It is important to remark that the percentages of butyl acetate degraded and volatilized shown in Table 4 do not add up to 100% because the complete mass balanced considered losses due to sampling that were not ascribed either to volatility of degradation.



**Figure 5.** Compounds time course and cell concentration profile for the solid–liquid TPPB using a polymer mixture of NBR and tire rubber. (a) Initial substrate concentration  $500 \text{ mg L}^{-1}$ ; (b) initial substrate concentration  $1000 \text{ mg L}^{-1}$ .

## CONCLUSION

Polymer selection criteria based on first principles thermodynamic methods were tested against measured partition coefficient values to determine which method(s) could effectively identify polymers for the simultaneous sequestration and degradation of phenol and butyl acetate in solid–liquid TPPBs. The criteria were based on polymer accessibility (polymer  $T_g$  and crystalline fractions) and the thermodynamic affinity between the polymers and the target molecule, as predicted by Hildebrand SPs and Hansen HSP, and activity coefficient estimates. HSP presented the best trends and offered some important insights into the resulting interactions between the polymers and the target molecules. The previously reported Hildebrand SP method showed greater scatter of the data and gave little insight about the possible interactions occurring in the system, perhaps due to the fact that it does not capture individual molecular interactions in the manner of the HSP method. Nevertheless, if applied to hydrophobic non-hydrogen-bonding solutes, it may still be a valuable tool for rational polymer selection.<sup>21</sup> Finally the activity coefficient method provided the anticipated trend, although the predicted PC values did not match the measured PC values well, and perhaps does not justify the use of this more complex method. It may, however, prove to be the best choice for systems in which truly ternary phase behaviour is anticipated, such as in the case of polymers that have some water-absorbing capacity or systems with extremely hydrophilic solutes, and for which binary interaction predictions (Hildebrand SPs and HSP) may be inadequate.

Pebax<sup>®</sup> 2355 was identified as the most suitable polymer due to its high PCs for both butyl acetate and phenol. This result was consistent with the high amorphous fraction and the results obtained with the HSP method. Biodegradation TPPB experiments performed with Pebax<sup>®</sup> 2533 showed improved performance compared with a previous report which used two target polymers

for the two solutes, and suggests that the Hansen HSP method may effectively select polymers for other applications.

The HSP method was applied to different waste polymers commonly found in commercial and laboratory environments. The polymer mixture of rubber tire and NBR selected proved to be very effective in consequent biodegradation experiments at higher polymer fractions, approaching the performance found with Pebax<sup>®</sup> 2355.

We continue to evaluate these three thermodynamic methods for predicting effective absorptive polymers over a range of solutes/polymers, with the goal of arriving at an overarching guide for other researchers who may wish to rationally select polymers for their TPPB applications.

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