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► **To cite this version:**

Marylène Vayer, Alexane Vital, Christophe Sinturel. New insights into polymer-solvent affinity in thin films. *European Polymer Journal*, 2017, 93, pp.132-139. 10.1016/j.eurpolymj.2017.05.035 . hal-02267763

HAL Id: hal-02267763

<https://hal.science/hal-02267763>

Submitted on 11 Jan 2022

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New insights into polymer-solvent affinity in thin films

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keyword: polymer thin film, Hansen solubility parameters, swelling, polymer-solvent affinity.

Abstract

Polymer-solvent affinity, estimated from the Hansen solubility parameters (HSP), was compared to experimental results of dissolution and swelling of polymer prepared in the specific form of thin film. This was carried out for 3 common polymers (PS, PLA, PMMA) and a series of 16 polar and non-polar solvents. The affinity properties predicted from the calculation of the relative energy distance (RED) values of most of the studied solvent/polymer pairs were in relative good agreement with the dissolution tests performed on the film. In contrast, no clear correlation between the RED and the swelling behavior was found. The observed deviations were attributed to the inability of the HSP theory derived from data acquired in polymer solutions to be extrapolated to the particular case of swollen polymer film.

1. Introduction

Whatever the application of polymers, from degradable packaging material to painting, chemical sensors to organic electronics devices, whatever the used processing method, the selection of the adapted solvent in regard to the considered polymer is a constant preoccupation. The behavior of a polymer versus a solvent or polymers together is of great importance. In general, the polymer-solvent affinity is partly driven by the interaction strength between them, the other part being driven by the entropy change on mixing.

A rather popular way to estimate the polymer-solvent affinity is to consider the Hildebrand solubility parameters (δ) introduced in 1950 [1]. These solubility parameters δ of species (polymer or solvent) describe the attractive strength between the molecules of the same species and are defined as the square root of the cohesive energy density and related for solvents to the energy of vaporization per volume unit. Since Hildebrand solubility parameters are only applicable to non-polar systems, Hansen proposed to extend the concept to polar systems by the introduction of three parameters in 1967 [2]. In Hansen's approach, the total solubility parameter (HSP) of a species is divided in three parameters, δ_d which represents the contribution of dispersion forces, δ_p polar interactions and δ_h H-bond formation to the total solubility parameter of the species. These solubility parameters components are estimated from direct experimental measurements (such as surface tension, refraction index etc) [2], [3], [4], [5] or theoretical methods such as groups contribution methods (most popular group contribution methods are Small, Hoy and Van Krevelen and Hoftyzer [6]) [7].

The polymer-solvent affinity is then evaluated from the difference of solubility parameters of the considered species that can be directly correlated to the Flory-Huggins parameter χ [2],

[8], [9], [10], [11], [12] or used to express the relative energy distance (RED) which is defined as the ratio of HSP Distance by Sphere Radius [2], [13], [14].

When the solubility parameters difference between the polymer and the solvent is small, the polymer-solvent affinity is high, which translates either in low values of χ or RED values <1 . Because the solubility parameters for most organic solvents are now tabulated, predicting polymer-solvent affinity using the Hildebrand or modified Hansen approach is a popular method which has been used successfully by numerous researchers. Agrawal et al. [14] for example classified the solvents for poly(lactide), poly(glycolic acid) and poly(esterimide) into two categories, solvents and non-solvents. Özdemir and Güner [7] distinguished between solvents in which the poly(ethylene oxide) is soluble or not soluble. However, as pointing out in particular by Lindvig et al. [11], if the Hansen solubility parameters values (δ) for solvents are well established, the set of solubility parameters for the polymers varies strongly depending on the authors [11], [15]. The use of Hansen approach is thus questionable or needs experimental confirmations.

In polymer thin film field, solvents are used into two main steps: i) for deposition purposes such as spin coating, dip coating, solution blow spinning etc.. where a solution of polymer in a solvent is used [13], [16], [17], [18], [19], [20] ii) for film post processing such as solvent vapor annealing (SVA) where solvent molecules in vapor state go into the polymer film [15], [21], [22], [23], [24]. In the specific area of block polymer thin films, the solvent selectivity is often a key parameter in the post-processing step that drives the ordering and orientation of the morphologies formed by the block polymer self-assembly, as well as order-order (and/or order-disorder) transition when one of the block is strongly swollen [22]. For this reason, the estimation of the polymer-solvent affinity is of major importance, allowing to predict the relative swelling of the different phases. However, because the strength of the solvent/polymer interaction can depend on concentration [15], [18], the picture obtained by

considering the solubility parameters that are generally derived from a situation where the polymer concentration is low, may not reflect the specific behavior in polymer thin film swelling where the concentration of polymer in the film is generally not under 20 %. Despite this trend has been already highlighted by several authors [15], [25], [26], the prediction of polymer-solvent affinity in thin films using solubility parameters still remains popular, even in previous works from our group [22].

In the present contribution, we propose to confront the polymer-solvent affinity, estimated from the solubility parameters, to experimental results of dissolution and swelling of polymer prepared in the form of thin films. This was carried out for 3 polymers (PS, PLA, PMMA) and a series of 16 polar and non-polar solvents. We used for that purpose, firstly the comparison of the 3 Hansen Solubility Parameter components of polymer and solvent, secondly the test of dissolution of thin films of polymer by solvent, thirdly the swelling of the polymer thin films in a controlled solvent vapor atmosphere.

2. Experimental methods

2.1. Materials

Poly(styrene) (PS), poly((D,L)lactic acid) (PLA) and poly(methyl methacrylate) (PMMA) with molar weights of 170 and 60 for PS, 95 and 20 for PLA and 350 and 36 kg.mol⁻¹ for PMMA were used and were named respectively PS 170K, PS 60K, PLA 95K, PLA 20K, PMMA 350K, PMMA 36K. PS were purchased from Sigma Aldrich, PMMA from Polymer source and PLA from Akina, Inc. All the used solvents were purchased from Sigma Aldrich and used as received.

2.2 HSP theoretical calculation

In Hansen's approach, the total solubility parameter of a compound can be divided in three parameters, δ_d the contribution of dispersion forces, δ_p the contribution of polar interactions and δ_h the contribution of H-bond formation to the total solubility parameter δ_t of the compound. The corresponding equation is :

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (1)$$

HSP contributions for solvents are primarily determined from their refractive index (for δ_d), dipole moments (for δ_p) and group contribution methods (for δ_h) [2].

A measure of the polymer-solvent affinity can be provided considering the sum R_a of the 3 differences between the solubility parameters contributions (d, p, h) between the polymer and the solvent [2], [11], [14], as defined using equation 2 (where $\delta_{d,s}$, $\delta_{p,s}$ and $\delta_{h,s}$ are the solubility parameters of solvents and $\delta_{d,p}$, $\delta_{p,p}$, and $\delta_{h,p}$ are the solubility parameters of polymer) and compared to a limit value R_o which is the radius of the sphere which contains the good solvents. The Relative Energy Difference (RED) is defined in equation 3. When RED is less than 1, the solvent is a good solvent of the polymer. Above 1, the solvent is considered as a non-solvent. Around this limit (RED comprise between 0.9 and 1.1), the solvent is considered as a intermediate solvent.

$R_a^2 = \left(4 * (\delta_{d,s} - \delta_{d,p})^2 + (\delta_{p,s} - \delta_{p,p})^2 + (\delta_{h,s} - \delta_{h,p})^2 \right)$	(2)
$RED = R_a/R_o$	(3)

2.2. Polymer thin film preparation

Si(100) substrates of 10*10 mm² were cleaned by sonication in dichloromethane, methanol and distilled water for 10 minutes each. Solutions of PS, PLA and PMMA were prepared as follows: polymer was weighted and dissolved in 1,2 dichloroethane to obtain a concentration of polymer of 15 mg.mL⁻¹. The solution was stirred at least 2 hours. Thin films were

deposited by spin-coating on Si substrates at 2500 rpm for 30 seconds. The film thicknesses ranged between 100 and 150 nm.

2.3 Thickness measurement using interference-based system

The film thickness was measured using an interference-based film thickness measurement system (F20, Filmetrics). The film was illuminated with a normal white light source. The intensity of the reflected light was recorded as a function of the incident wavelength and was fitted using a model which takes into account the interferences of the light waves reflected from the upper and lower surfaces of the film at different light wavelengths. Knowing the optical refraction and extinction indexes of the material constituting the thin film as a function of the light wavelength allows to determine the film thickness. The optical indexes of the polymer film as a function of the light wavelength were determined by ellipsometry. The accuracy of the determination of the thickness was verified on polymer films using Atomic Force Microscopy measurement of the depth of the scratch line, which allows also the determination of the thickness of the polymer film.

2.4 Dissolution tests

In the dissolution tests, one drop of solvent was deposited onto the sample and flushed out after 2 seconds using a nitrogen stream. The polymer-solvent affinity was estimated on the basis of the removal of the polymer layer in place of the solvent drop. A visual inspection allows to give a first insight on the affinity (total removal of the film or not). To conclude more precisely on the dissolution, the sample was gently scratched before the test and the sample was then observed with optical microscope. If no scratch was observed, the film had been flushed out with the solvent and the solvent was classified as solvent for the considered

polymer. If the scratch still remained on the surface, the solvent was classified as non-solvent (or intermediate solvent) for the polymer. In this later case, AFM was used to determine the thickness reduction and discriminate between intermediate solvent and non-solvent.

2.5 Evaluation of the in-situ swelling of polymer thin films

The swelling of polymer thin films was achieved by exposing the polymer thin films to solvent vapors. For that purpose, a closed PTFE box with a cover equipped with a sealed optic glass window was used. A container filled with the solvent to study was disposed in the closed box. The vapor pressure in the PTFE box was controlled by blending the solvent with a miscible compound that modulates the vapor pressure. We mainly used for that purpose squalane, which has a negligible vapor pressure. The solvent vapor pressure above the squalane solution was in this case calculated using the Raoult law. For the solvent non miscible with squalane (acetone, acetic acid, DMSO and alcohols) water was used since water is a non-solvent for all tested polymers. The vapor pressure determined in this case took into account the non-ideality of the mixture [27], [28]. The glass window allows thin film color inspection and thickness determination using interference-based system during solvent vapor exposure. The swelling ratio d/d_0 is defined by the ratio between the thickness (d) of the film at time (t) and the thickness (d_0) at time ($t=0$).

3. Results and discussion

3.1 HSP polymer-solvent affinity evaluation

Table 1 displays the different contributions of the total solubility parameters for the tested solvents and the polymers given by Hansen [2]. Although the proposed values for solvents are

the objects of a relatively large consensus, the HSP components proposed by Hansen for polymers do meet a so general agreement [12], [14], [15], [29].

	δd	δp	δh	δt
acetic acid	14.5	8	13.5	21.4
acetone	15.5	10.4	7	19.9
chlorobenzene	19	4.3	2	19.6
chloroforme	17.8	3.1	5.7	18.9
cyclohexane	16.8	0	0.2	16.8
1,2 dichloroethane	19	7.4	4.1	20.8
dichloromethane	18.2	6.3	6.1	20.2
1,4 dioxane	19	1.8	7.4	20.5
dimethyl sulfoxide	18.4	16.4	10.2	26.7
ethanol	15.8	8.8	19.4	26.5
ethyl acetate	15.8	5.3	7.2	18.2
methanol	15.1	12.3	22.3	29.6
2, propanol	15.8	6.1	16.4	23.6
tetrachloroethylene	19	6.5	2.9	20.3
tetrahydrofuran	16.8	5.7	8	19.5
toluene	18	1.4	2	18.2
PS	18.5	4.5	2.9	21.4 (8)
PLA	18.6	9.9	6.0	19.9 (10.7)
PMMA	18.6	10.5	5.1	19.6 (8)
Table 1: Hansen solubility parameters ($J.cm^{-3}$) ^{1/2} for solvents and polymers. In bracket are given for the polymers the radius of the solubility sphere [2].				

Table 2 gives the RED values for all the considered pairs solvent/polymer in the columns (1), (2), (3). According to this table, good solvents for PS are chlorobenzene, chloroform, cyclohexane, 1,2 dichloroethane, dichloromethane, 1,4 dioxane,

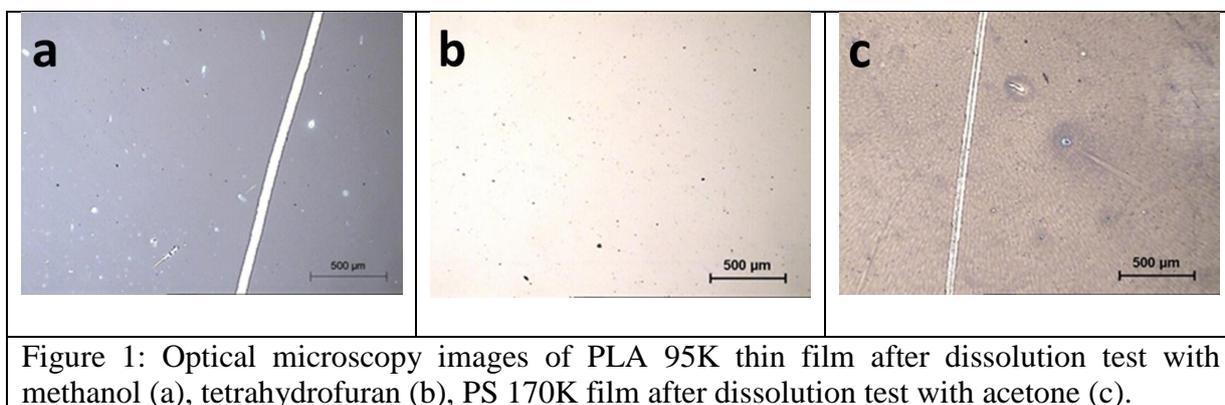
tetrachloroethylene, tetrahydrofuran and toluene. Non-solvents are acetic acid, acetone dimethylsulfoxide and alcohols (methanol, ethanol, 2, propanol). Ethyl acetate is an intermediate solvent. Non-solvents for PLA are alcohols, intermediate solvents are acetic acid, cyclohexane and toluene, and the other tested solvents are good solvents. For PMMA, non-solvents are acetic acid, cyclohexane, alcohols and toluene. Chlorobenzene, chloroform, 1,4 dioxane, dimethylsulfoxide and ethyl acetate are intermediate solvents. The other evaluated solvents are good solvents. Note that we could also have considered the values of the Flory-Huggins parameters in order to estimate the affinity polymer-solvent. But because those parameters would have been calculated using the same HSP parameters values, it would have led to similar conclusions.

	RED(PS) (1)	RED(PLA) (2)	RED(PMMA) (3)	D(PS) (4)	D(PLA) (5)	D(PMMA) (6)	SR(PS) (7)	SR(PLA) (8)	SR(PMMA) (9)
acetic acid	1.7	1.1	1.5	non	good	good	1.1	2.4	2.7
acetone	1.2	0.6	0.8	intermediate	good	good	1.4	3.0	4.4
chlorobenzene	0.2	0.6	0.9	good	good	good	1.8	1.8	1.8
chloroform	0.4	0.7	0.9	good	good	good	1.6	2.3	2.8
cyclohexane	0.8	1.1	1.5	intermediate	non	non	1.5	1.0	1.0
1,2 dichloroethane	0.4	0.3	0.4	good	good	good	1.8	2.8	2.6
dichloromethane	0.5	0.3	0.5	good	good	good	1.6	2.2	2.1
1,4 dioxane	0.7	0.8	1.1	good	good	good	2.4	4.0	2.8
dimethylsulfoxide	1.7	0.7	1.0	non	good	intermediate	1.1	2.0	1.4
ethanol	2.2	1.4	1.9	non	non	non	1.1	1.3	1.1
ethyl acetate	0.9	0.7	1.0	good	good	good	1.7	2.7	2.0
methanol	2.7	1.7	2.3	non	non	non	1.1	1.2	1.2
2 propanol	1.8	1.2	1.7	non	non	non	1.0	1.1	1.2
tetrachloroethylene	0.3	0.4	0.6	good	non	non	1.4	1.2	1.0
tetrahydrofuran	0.8	0.5	0.8	good	good	good	1.6	1.8	1.6
toluene	0.4	0.9	1.2	good	good	good	1.6	1.6	1.4

Table 2: (1), (2), (3) Relative energy distance of all the considered solvent (s)/polymer pairs for PS, PLA and PMMA. The solvents are classified into good solvents, (RED < 0.9) in green, non-solvents (RED > 1.1) in red, and intermediate solvents (0.9 ≤ RED ≤ 1.1); (4), (5), (6): solubility results using the dissolution of polymer thin films by a drop of solvent. The solvents are classified into good solvents (all the film is flushed away, in green); non-solvents (the film remains intact, in red); intermediate solvents (the film is still present but its thickness has decreased as measured by AFM, in orange); (7), (8), (9): swelling ratio (SR) of the polymer films in the tested solvent vapors for an exposure partial pressure of 0.85. The solvents are classified into good solvents (SR > 1.5) in green ; non-solvents (SR < 1.3); intermediate solvent (SR ≈ 1.4 in orange).

3.1 Dissolution tests

The dissolution of the polymer thin films was tested with the 16 solvents. A typical example, PLA 95K film dissolution test with methanol and tetrahydrofuran, is presented in figure 1. With methanol, the film remained unchanged (figure 1a) indicating that methanol was a non-solvent of PLA 95K. With tetrahydrofuran, the film was totally removed as seen in figure 1b. This led to the conclusion that tetrahydrofuran was a solvent of PLA 95K. Intermediate cases were observed as for example acetone dissolution of a PS 170K film. In this case, the film remained on the surface but the thickness of the film decreased, indicating a partial dissolution of the film. The solvent could be classified as intermediate solvent.



The observed results do not depend on the molecular weight of the polymer, and are presented in table 2 for PS, PLA and PMMA in columns (4), (5), (6). These results allow to define three groups of solvent for each polymer: a group of good solvents, non-solvents and intermediate solvents. For polystyrene, the good solvents are chlorobenzene, chloroform, 1,2 dichloroethane, dichloromethane, 1,4 dioxane, ethyl acetate, tetrachloroethylene, tetrahydrofuran, toluene, the non-solvent are acetic acid, acetone, dimethylsulfoxide, alcohols. For PLA and PMMA, non-solvents are alcohols, cyclohexane and tetrachloroethylene. Intermediate solvents are acetone and cyclohexane with PS and dimethylsulfoxide with PMMA.

3.2 Swelling experiments results

Figure 2 shows two typical behaviors of the swelling ratio recorded during 1,2 dichloroethane vapor exposure of PS 170K and PLA 90K films (with the same initial thickness of 125 nm) at a partial vapor pressure of 0.95. In the case of PS film, the film swelled up to a plateau which was reached after 2000 s exposure. After drying, the uniformity of the film was preserved as judged from figure 2b. In the case of PLA film, the film swelled up to a maximum after 700 s and dewetted as can be seen in optical microscopy (figure 2c) leading to a meaningless value of 1.4 for the swelling ratio.

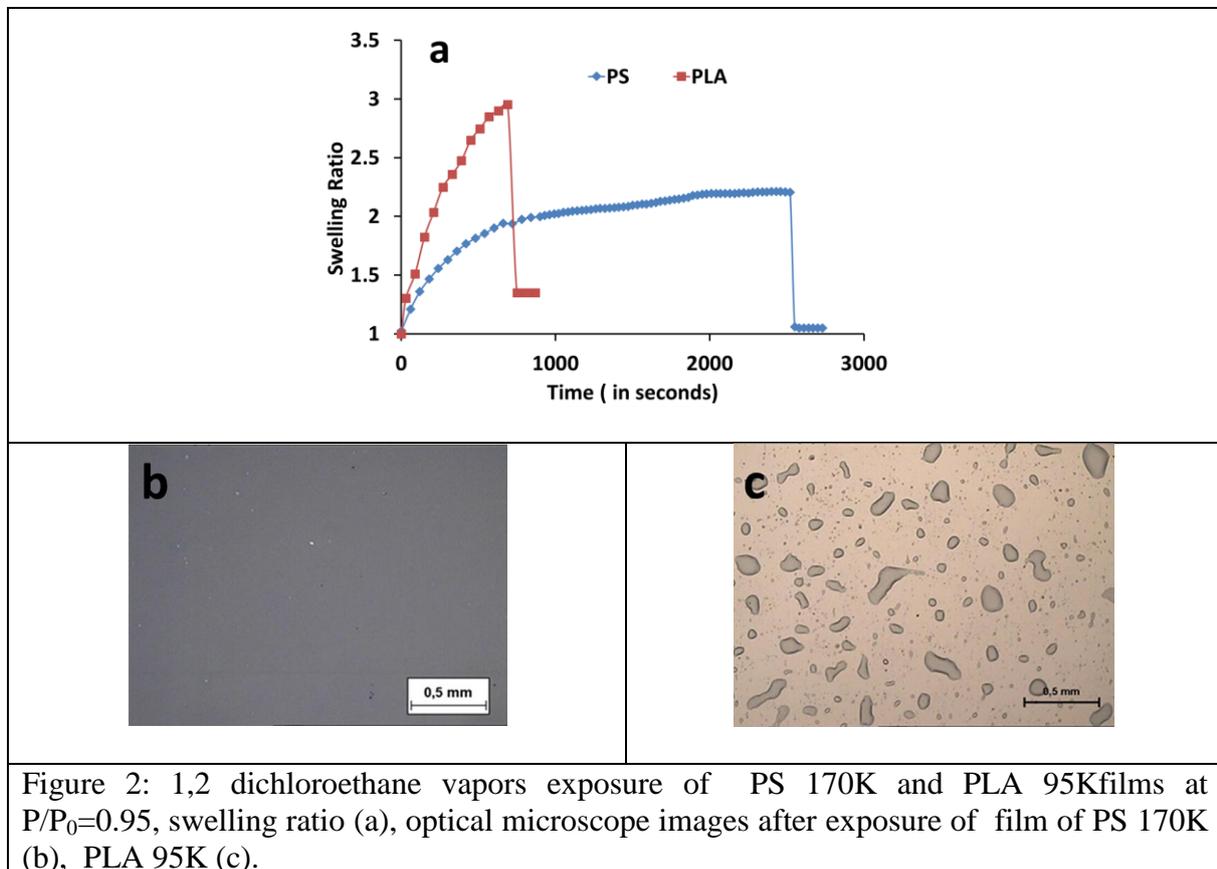
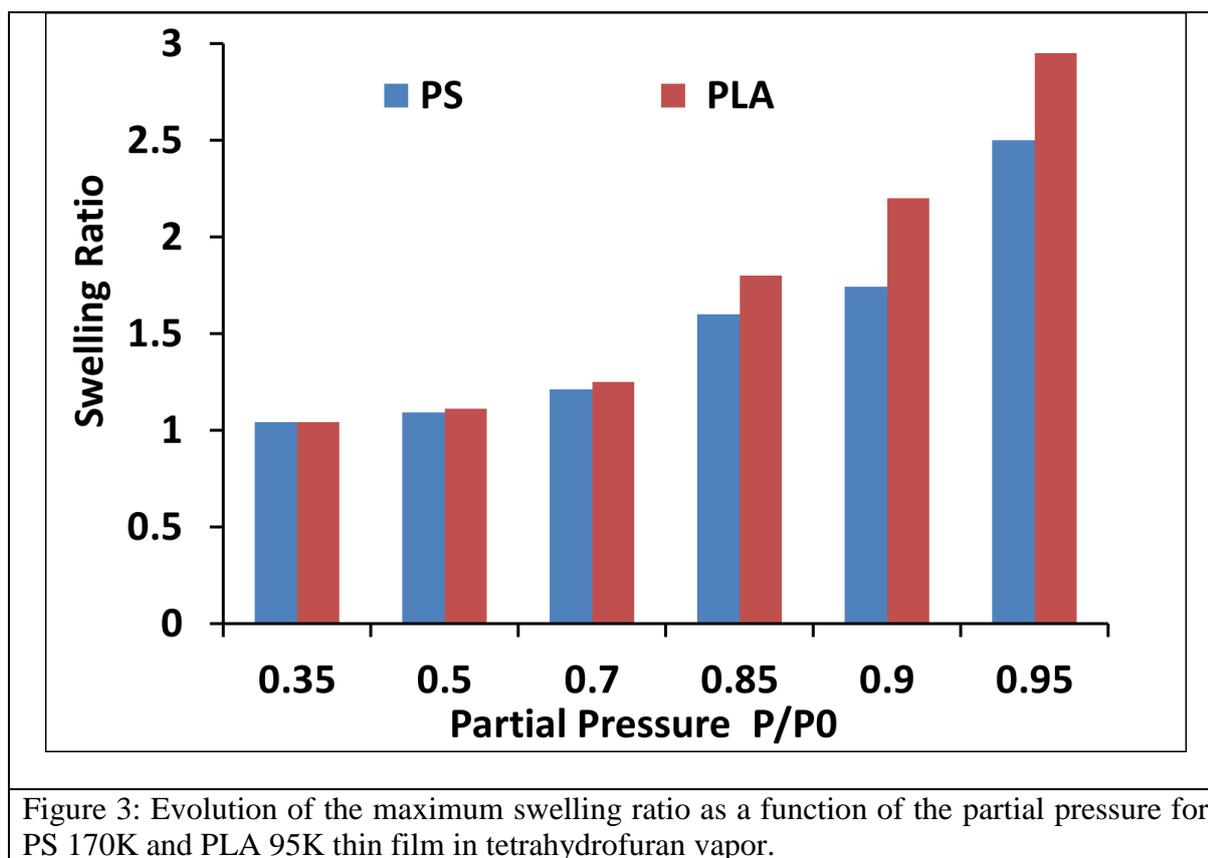


Figure 2: 1,2 dichloroethane vapors exposure of PS 170K and PLA 95K films at $P/P_0=0.95$, swelling ratio (a), optical microscope images after exposure of film of PS 170K (b), PLA 95K (c).

Figure 3 shows the evolution of the maximum of swelling ratio curve as a function of the partial pressure for PS 170K and PLA 95K film exposed to tetrahydrofuran vapor. As the partial pressure increases, the swelling ratio increases up to the dewetting of the film. In this case, the dewetting occurred for partial pressure higher than 0.97.



As exemplified in this figure, to discriminate the ability of solvent to swell polymer, the swelling ratio and consequently the partial pressure must be as high as possible without leading to dewetting of the film. A pressure partial pressure of 0.85 was selected to compare the swelling behaviors of the different polymers. This value is the highest one we could use without any dewetting of the studied polymers. The films of PS 60K and PS 170K exhibited the same behavior and led to the same swelling ratios. This observation was also valuable for PLA 20K and PLA 95K, and for PMMA 36K and PMMA 350K and led to the conclusion that the molecular weight in the chosen range does not modify the swelling ratio. It should note that films based on polymer with lower molecular weights (typically less than 10K) dewetted rapidly, preventing observation of swelling behavior.

The table 2 presents the swelling ratios for PS, PLA and PMMA at a partial pressure 0.85 in columns (7), (8), (9). At this partial pressure, all the swelling ratios are comprised between 1 and 4.4. The PS film swells always less than PLA and PMMA films except with cyclohexane and tetrachloroethylene. In the other solvents, the swellings of PLA and PMMA films are more important than for PS. Except for acetic acid, acetone and chloroform the swelling is more important for PLA than PMMA. For toluene, the swelling ratio increased from PMMA < PS \approx PLA.

3.3 Discussion

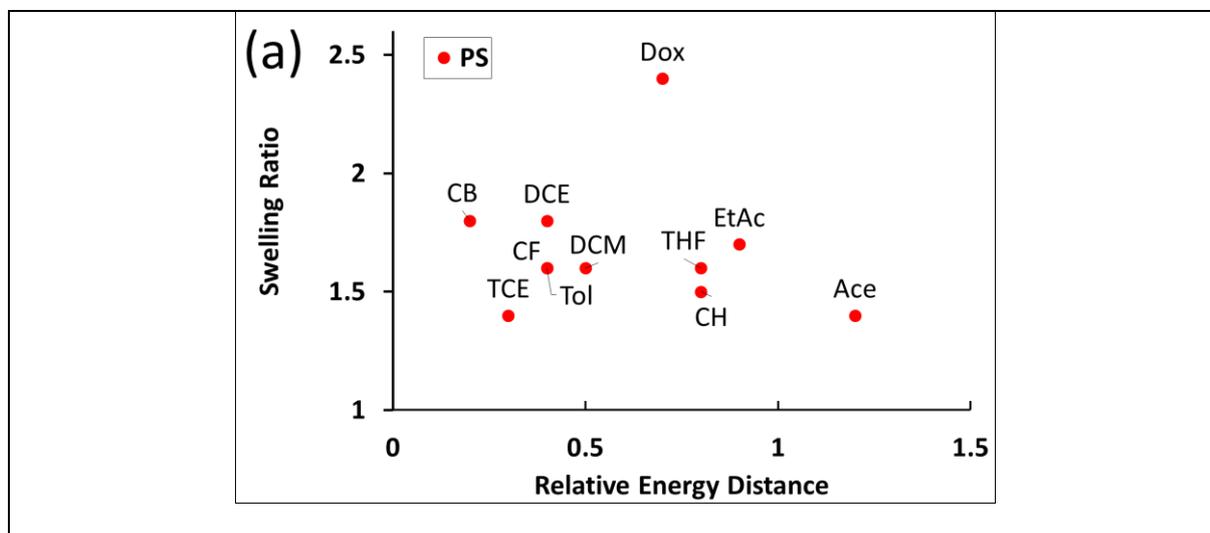
Polymer-solvent affinity

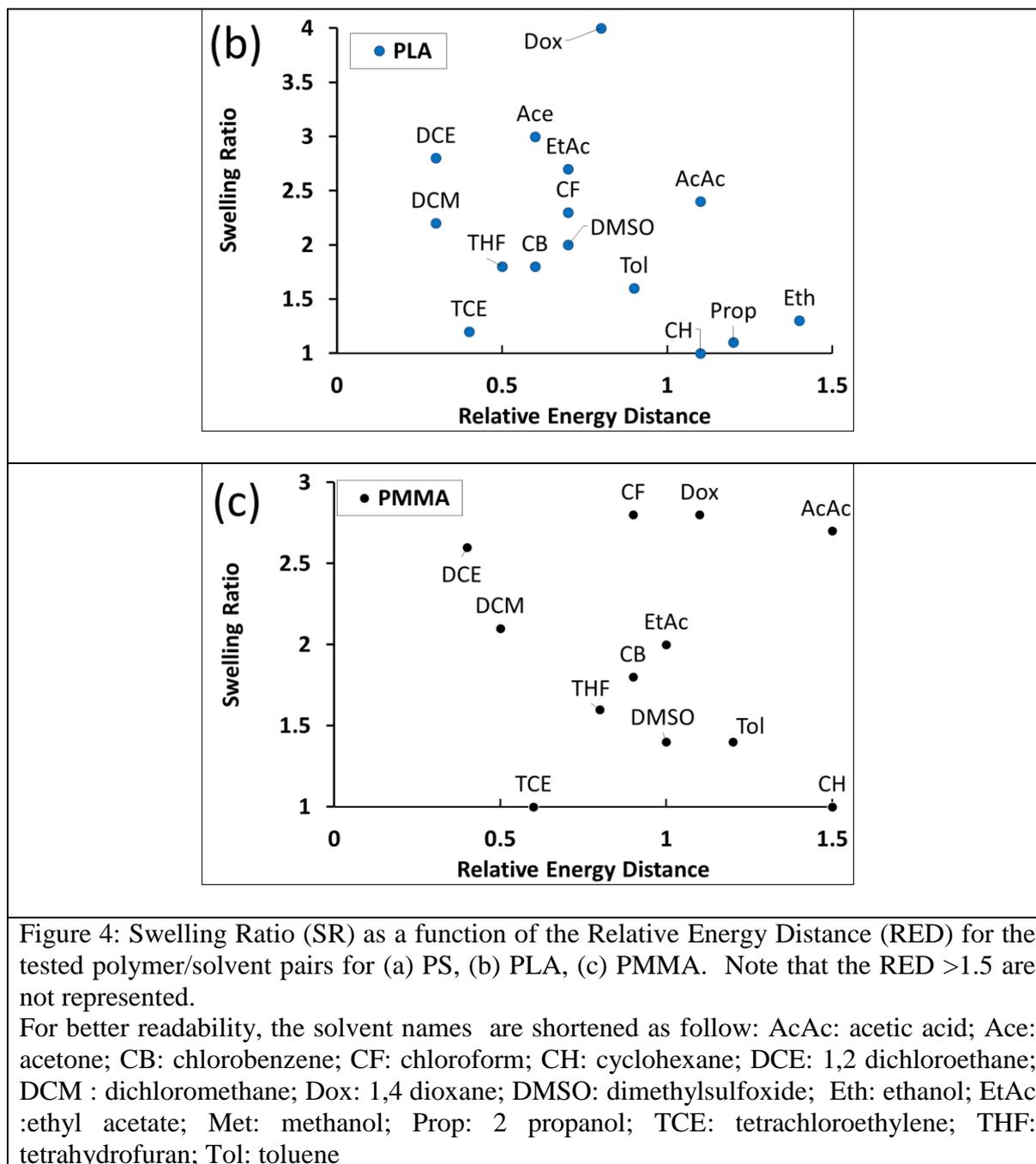
As seen in table 2, the polymer-solvent affinities predicted with the calculation of the RED values of most of the studied solvent/polymer pairs are in relative good agreement with the dissolution tests and the swelling experiments. For values of RED distances > 1.1 , the polymer/solvent pairs have no affinity as judged by the negative dissolution test and the limited polymer swelling (SR ranging from 1 to 1.3). Conversely, RED distances < 0.9 are consistent with polymer dissolution and swelling ratio > 1.4 . Discrepancies have however been observed in several cases. For example, PMMA was found to have experimentally high affinity with acetic acid with a high swelling ratio (2.7) whereas the RED distance is largely above unity (1.5). Also in contradiction, PLA was not dissolved and was only slightly swelled (SR=1.2) with tetrachloroethylene whereas the RED distance is 0.4. Other discrepancies between HSP prediction and experiments are visible by non-matching colors in table 2. The inability of the HSP model to predict the polymer-solvent affinity in such cases is questionable. Probably we have to point out the uncertainty of the values of some of the solubility parameters, which ends to these discrepancies. These limitations render the simple dissolution test we used in this work very useful. The advantages of this method compared to

a classical dissolution test of bulk material in solvent are numerous. Firstly, a limited amount of material (in our case, 15 mg was used to prepare 1 mL of solution in 1,2 dichloroethane) could serve to prepare at least 20 substrates for this type of dissolution tests. Secondly, in contrast to dissolution in bulk where the conclusions are sometimes difficult to make (transparent jelly particles can sometimes be difficult to notice by eyes), the alteration of the film is easy to qualify and also, partial dissolution or dissolution kinetic can be obtained using thickness evolution determined by AFM.

Polymer-solvent affinity and swelling ratio

In order to push further the examination of the affinity polymer-solvent, we have plotted the swelling ratio as a function of the RED value for each of the three polymers in figure 4 (note that we have removed from this graph the results that exhibit RED > 1.5).





Under the assumption that the SR of a solvent/polymer pair will increase with higher polymer- solvent affinity (higher solvent amount uptake), we expect to observe a monotonic increase of the SR with decreasing RED values. As seen on these graphs, there is not a clear correlation between the RED and the swelling behavior. As a matter of fact, the prediction of the relative swelling of a given polymer exposed to various solvent vapors is highly

inaccurate. Similarly, the comparison of the RED values for a given solvent repeatedly fails to predict the relative SR of different polymers. Maybe that the most striking example can be found with chloroform, which RED values with PS, PLA and PMMA are respectively 0.4, 0.7 and 0.9, suggesting a SR in the order PS>PLA>PMMA whereas the experimentally swelling levels are in reverse order.

Limitation of the HSP theory

The relative disagreement between measured and predicted swelling behaviors in this work underlines the limitation of the HSP theory to specifically describe the behavior of solvent/polymer interaction in the case of swollen thin film. We herein propose some conceptual explanations to account for such deviations.

Firstly, it has to be considered that the HSP theory is derived from data acquired in polymer solutions within the limit of infinite dilution, [2] which is not the case in the particular case of swollen polymer film. Even for high swelling ratio, the polymer fraction (PF) is still high (PF=0.5 for SR=2). It is known that polymer-solvent affinity can show great variation between the diluted and concentrated solutions [3], [25], [26], [30] that renders the extrapolation of polymer-solvent affinity difficult to make in such highly concentrated system. This compositional dependence was demonstrated to be both entropy and/or enthalpy driven, depending on the polymer/solvent pair [31].

Another consideration that can account for inconsistency of the HSP approach in the polymer thin film area is the fact the swelling is a complex behavior that results not only from polymer-solvent affinity but also from the ability of the polymer to deform. The change of energy due to absorption of a liquid by a polymer can be considered as sum of contributions

due to deformation of the polymer and mixing of a polymer with the liquid. Even if the mixing is favorable for enthalpic and entropic reasons, the solvent uptake by the polymer phase is influenced by the visco-elastic deformation of the film. Depending on the polymer characteristics, this effect can be more or less important leading to swelling result that can be seemingly inconsistent with the polymer-solvent affinity. This effect that has been extensively examined in the case of swelling of crosslinked-gel [32] is far from being well understood in the case of solvent vapor annealing. Presumably physical crosslinking in linear polymers plays the role of the chemical crosslinking up to a point where the solvent concentration is large enough to provoke a massive disentanglement of the macromolecules (and a macroscopic dewetting of the film). Deeper experimental and numerical investigations are currently undertaken in our group in order to address this problem.

By now, our conclusions are to recommend the actual thickness variation measurement under solvent vapor exposure in order to better evaluate the relative volume change of different polymer systems upon solvent vapor exposure.

Acknowledgements:

This project is supported by the region “Centre” through the SUSCRYPP project. We would like to acknowledge the “S2E2 pole de compétitivité” for its endorsement. We would like to thank Joel Puibasset for fruitful discussions. M.H. Hillmyer is acknowledged for his suggestion to use the squalane as a way to control the solvent vapor pressure.

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