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Polyethylene Slurries: Swelling and Solubility

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Abstract

The solubility of different alkanes in polyethylene (PE) of different densities, as well as the solubility of the polymers in the alkanes, and the degree of swelling of the powders were studied as a function of temperature. It was found that the solubility of linear low density polyethylene (LLDPE) was as much as 6 times greater than that of High Density Polyethylene (HDPE) at the same temperature, and that LLDPE swelled at least 50% more than HDPE the same diluent at the same temperature. The breakthrough curves also showed that lighter alkanes swell the PE more at a given temperature than do the heavier ones, and that the breakthrough points (the temperature at which the swelling vs temperature curves change slope) occur at lower temperatures for PE of lower density. Gel formation is observed for medium and low density polyethylenes in pentane and hexane. This quantitative information will be useful in developing process models for different industrial polymerization processes, as particle swelling can have a significant impact on slurry viscosity and the flow stability and solids loading of commercial reactors.

Key Words : polyethylene, slurry, swelling, solubility of alkanes, breakthrough curves

1 Introduction

The solubility and swelling of polyethylene by gaseous components in binary (polymer plus one penetrant),^[1,2,3,4,5,6,7,8,9,10] ternary (2 penetrants),^[2,4,5,11,12,13,14,15] and more recently quaternary^[16] (3 penetrants) systems have been the object of several studies over recent years. While the dissolution of a polymer in a solvent can be viewed as a dispersion of the individual macromonomers in a continuous medium, the swelling of the same polymer is slightly more complex. The act of dissolving a small molecule – here an alkane such as those used in industrial processes – in a semicrystalline polymer at a state below its melting point results in a measurable change in the volume of the mixture, and causes the polymer to transition from

an unsolvated glass state to a solvated, expanding rubbery state.^[17] The extent to which this occurs will depend on the interaction between the polymer and penetrant molecules.

It has been demonstrated that the swelling of the amorphous phase of polyethylene (and polypropylene) can have a major impact on the solubility of different species, and thus on the rate of polymerization, and on polymer properties in gas phase polymerizations. Furthermore, it can also have an impact on the crystallization of the polymer, which in turn can impact rates of transport and particle morphology during a polymerization process.^[18] Despite the fact that slurry phase polymerization processes remain an economically important means of making polyethylene (PE), it turns out that very few studies have been performed concerning the sorption of liquid diluents in polyethylene, the polymer swelling by the liquid penetrants, and the solubility of PE in the same liquid diluents. This is crucial thermodynamic data for slurry (and eventually solution) polymerization, as well as for design and operation of purification equipment.

Obviously, the swelling of the polymer by the diluent, and the eventual dissolution of the polymer in the continuous phase are both going to be important points when developing an in-depth understanding of a slurry process. Polymer dissolved at the bulk temperature of the reactor could easily deposit on heat transfer surfaces and reduce the ability to remove the heat of reactor, deposit on pumps or agitators, or in the case of loop reactors, lead to large pressure drops, slug formation and reactor instability.^[19]

The temperature sensitivity of these two phenomena will also be important, and it is expected that slurries will exhibit a different temperature response than gas phase systems.^[20] As with gas phase reactions, increasing temperature can lead to higher catalyst productivity, but unlike in the gas phase, this also enhances the risk of polymer swelling since the latter tends to become more soluble in the continuous phase at higher temperatures.^[21] For instance, Aminabhavi and Naik^[22] studied the sorption of 14 organic liquids into high density polyethylene (HDPE) geomembranes at 25, 50 and 70°C, as well as the swelling of the HDPE geomembrane. They showed that increasing the temperature increases the sorption and diffusion of the organic liquids through HDPE, hence increasing the swelling of HDPE. Other studies showed that if the temperature reaches a critical point, polymer particles might swell significantly and form a gel or adhesive polymer slurry that can slow down circulation in the reactor or lead to deposition on the reactor wall.^[23:24]

PE can be swollen by a diluent, but it can also dissolve in the same liquid. Some studies have examined the solubility of polyethylene in different diluents. For example, De Loos et al.^[25] showed that cyclohexane is a better diluent than n-heptane which is a better diluent than n-hexane. Other studies have confirmed that shorter alkanes were in general better diluents at a given temperature than longer ones.^[26,27, 28] In terms of the solubility of LLDPE in different solvents, De Loos et al.^[25] found that longer chain alkanes were better solvents for the polymer and attributed this to the increasing similarity of the solvent and polymer molecules as the former grow longer. They also concluded that the solubility of the polymer increased for lower average molecular weight and density. Paricaud et al.²⁹ also showed that longer n-alkanes were better solvents for polyethylene. Buzedin et al.³⁰ compiled data on various Hansen solubility parameters of normal alkanes of different length and showed that the values of the solubility parameter diminishing as 1 over the number of carbons in the alkane chain, confirming this tendency.

In a similar vein, Krajakova et al.²⁶ studied the sorption of liquid diluents (i.e. n-octane, n-hexane, n-pentane) in different PE samples of varying density from 902 to 967 kg m⁻³. They showed that longer hydrocarbons diluents have higher solubility in all PE samples. But while they showed that the different PE were soluble in liquid diluents, this dissolution was not quantified. Finally, they also demonstrated that the density of the polymer is important in determining how the amorphous phase swells. They observed a significant increase of liquid n-alkane solubility in the polymer as the PE crystallinity decreases from 60 wt%, but that remained constant for crystallinities higher than 60 wt%.

The objective of this paper is to systematically quantify the solubility of diluents in different PE, the solubility of PE in diluents, and the swelling of the amorphous phase as a function of temperature for PE with different densities. These 3 quantities have not been reported together for the same polymers in the open literature and will be quite useful in future reactor simulations where partial polymer solubility is needed to quantify fouling and help calculate slurry viscosities. It is important to note here that reporting quantities such as swelling, and solubility (in the polymer) can be delicate. It is often assumed that the crystalline phase remains impervious to such phenomena. However, it has been pointed out, for instance by McDermott et al.³¹ that solvent uptake can occur at the grain boundaries of the crystals and provoke the dissolution of the smaller crystallites. This would mean that the quantity (and nature) of the amorphous phase of PE could change during the solubility and swelling experiments. While this is a real phenomenon, we will nevertheless make the explicit assumption that the relative

changes in the amount of amorphous phase will not have a first order impact on the results of the swelling experiments presented in the current work.

2 Experimental

2.1 Materials

Normal alkanes with carbon numbers 4 through 10 with a minimum purity of 99% were used as received from Air Liquide France. All seven alkanes were used for the swelling experiments, but only the n-pentane and heavier alkanes were used in the solubility experiments.

LLDPE powders were graciously supplied by Ineos (LLDPE-I), and HDPE and medium density polyethylene (MDPE) powders were graciously supplied by Borealis (HDPE-B, MDPE-B).

The crystallinity of the polymer samples was measured using differential scanning calorimetry (DSC 3+ by Mettler Toledo). Polyethylene samples were weighed (5-7 mg) and placed in an aluminium capsule with a volume of 40 μL . The sample was first cooled to -20°C and then heated from -20 to 180°C at a heating rate of $10^\circ\text{C min}^{-1}$, held for 5 minutes at that temperature and then cooled from 180 to -20°C at a rate of $10^\circ\text{C min}^{-1}$. This temperature was maintained for 5 minutes, and the sample was reheated to 180°C at a rate of $10^\circ\text{C min}^{-1}$. The melting behavior of the samples was studied in the second heating cycle to detect the melting point and the melting enthalpy of the samples. The ratio of the heat of fusion of the sample to that of the completely crystallized polyethylene was used to calculate the degree of crystallization. A heat of fusion of 293 J g^{-1} for completely crystallized polyethylene was used for the calculation. The STARE software was used for data acquisition and data analysis. Polymer densities and crystallinities are summarized in Table 1; along with the molecular weight data measured elsewhere.¹⁶

Table 1. Density, crystallinity, weight average molecular weight (MW) and polydispersity index (PDI) of the studied polymer samples

	Density (kg.m^{-3})	Crystallinity (%)	MW	PDI
HDPE-I	960	75	70 kDa	2.97
HDPE-B	945	65.7	245 kDa	10.9
MDPE-B	935	54.2	121 kDa	8.7

The polymers were used either in the form of pellets as received, or in hot pressed films. Samples of LLDPE-I, HDPE-B and MDPE-B were hot-pressed at 180°C for about 2 hours, and then cooled, in order to produce a thin film. The final circular film has a diameter of 20 mm and a thickness of 1 mm.

2.2 Dissolution of polyethylene in liquid diluents

It is known that amorphous PE and low molecular weight fractions of polymer can dissolve in liquid alkanes, and that the amount of polymer that dissolves will be a function of the temperature and alkane chain length. Furthermore, if we wish to study the swelling of PE by liquid alkanes, it is necessary to know what fraction of that PE actually dissolves in the liquid diluents.

To measure the PE solubility in alkanes, 5g of polymer is added to 15 mL of diluent in a test tube. This is the same ratio of polymer to diluent as was used in the reactor for the swelling experiments (see below), and is representative of lower limits of solid loading in industrial processes^[32]. A magnetic stirrer bar is inserted in the tube. The tube is then closed and kept at the desired temperature for 48 hours. After 48 hours the supernatant solution of diluent and polymer is withdrawn with a syringe and weighed. The solution is left to dry under a fume hood for 24 hours, and then in an oven at 100°C for an additional 24 hours and weighed again. Each experiment was repeated 2-3 times. The amount of dissolved polymer (g of polymer dissolved / g of diluent) is calculated as follows:

$$S_{PE}^{diss} = \frac{m_{caps+PE,d} - m_{caps}}{m_{caps+sol} - m_{caps+PE,d}}$$

Where $m_{caps+PE,d}$ is the mass of the capsule with the dried PE, $m_{caps+sol}$ is the mass of the capsule with the supernatant solution of diluent and polymer and m_{caps} is the mass of the empty capsule.

2.3 Solubility of Alkanes in PE

2.3.1 Room temperature sorption

PE pellets and films were used for the sorption experiments as they are more easily recovered than powder from the liquid phase. The procedure for the alkane solubilities is similar to that reported by Krajkova et al.^[33] and relies on first saturating a PE sample, and then measuring the weight loss as it dries. To do so, a PE film or granule is weighed and placed into a given diluent for 48 hours (it was found that increasing the sorption time to more than 48 hours does not have any measurable difference). After reaching equilibrium, the polymer sample is removed from the liquid, any droplets present on the surface of the film/granule are rapidly dislodged by lightly sponging it with a filtration paper, and the polymer sample is placed on an analytical balance. The rate of decrease of the mass of the polymer at room temperature was recorded manually until a stable value was observed. The solubility of the liquid diluent in the polymer is calculated as follows:

$$S = \frac{m(t = 0) - m_{PE_{end}}}{m_{PE_{end}}}$$

Where $m(t = 0)$ is the mass of the swollen polymer measured at zero time before the desorption and $m_{PE_{end}}$ is the mass of the dry polymer after the desorption experiment.

Generally, the dry polymer mass after the experiment is found to be lower than the mass of the dry polymer before the experiment. The reason is that a fraction of the polymer partially dissolves into the liquid diluent during the sorption experiment. The dissolution of the amorphous phase of the polymer in the different diluents is therefore considered when calculating the solubility of the different liquid diluents in the polymer.

2.3.2 Sorption at process temperatures

Only HDPE-I was evaluated in this manner. For each experiment, one granule was introduced into a given liquid diluent at different temperatures for 48 hours as previously. After reaching equilibrium, the granule (approximately 11 mg) is pulled out of the liquid, its surface is quickly dried by a filtration paper and placed in a 40 μ L steel capsule used for thermogravimetric analysis (TGA). The decrease of the mass of the capsule as a function of temperature was measured using a TGA 2 by Mettler Toledo. The advantage of this technique is that if the solid sample is transferred to the capsule rapidly enough, the desorption is carried out at the same

temperature as the sorption. Isothermal analysis at the temperature of interest without any nitrogen atmosphere flow was performed. The values obtained in the desorption analysis were treated using STARe Software.

All the experiments were carried out three times at the same conditions (identical temperature, PE granules) and were found to be quite repeatable. The solubility S is calculated as for solubility experiments at room temperature

At high temperatures, the dry polymer mass after the experiments is very different from the mass of the polymer before the desorption experiment since the dissolution of the polymer in the diluents is greater with temperature. It is therefore crucial to consider PE dissolution in the diluents when measuring the solubility at high temperatures.

2.4 Swelling Experiments

2.4.1 Bulk Swelling

The bulk swelling method was used for the majority of the swelling measurements presented in this paper. HDPE-B, MDPE-B and LLDPE-I powders were used for the swelling experiments in order to show the effect of the crystallinity of the PE sample on its degree of swelling, as well as the process temperature. The vessel used for the swelling experiments is a 2 liter stirred reactor heated by circulating water in an external jacket. A sapphire window is available on this reactor in order to see the volume change due to the polymer swelling during the sorption experiment. A known amount of polyethylene powder (± 300 g of polymer) and diluent (± 900 mL) are introduced in the reactor. The powder is allowed to settle (usually a question of a minute or so), and the height of the powder bed is measured. The reactor is then closed and heated to the desired temperature. The reactor is stirred at a constant temperature for 90 minutes (the time it was found to reach equilibrium) and the value of the height of the powder is then taken once again. The experimental temperature dependent swelling is then calculated in % of volume change, as follows:

$$SW_{\text{exp}} (\%) = \frac{h(T) - h(T_i)}{h(T_i)} \times 100$$

Where $h(T)$ is the height of polymer powder inside the reactor at different temperature steps taken from the sapphire window and $h(T_i)$ is the height of polymer powders inside the reactor at the beginning of the experiment at room temperature taken from the sapphire window.

However, the swelling of the polymer has to be corrected for the partial dissolution of the amorphous phase of the polymer in the liquid diluents, especially for light diluents (i.e. n-pentane, n-hexane), as have been seen in Section 2.2. This correction is achieved by adding the volume of polymer dissolved in the diluent, V_{PE}^{diss} , to the volume of swollen polymer measured during swelling experiments, V_{PE}^i . Furthermore, this volume of swollen polymer measured experimentally must be corrected for polymer expansion due to temperature increase, $V_{PE,corr}^i$ using the linear thermal expansion coefficient of LLDPE34

$$V_{PE,corr} = (V_{PE,corr}^i + V_{PE}^{diss}) \left(\frac{SW_{exp}}{100} + 1 \right)$$

$$\underline{V_{PE,corr}^i} = V_{PE}^i \times \frac{\rho_{PE}^{am}(T_i)}{\rho_{PE}^{am}(T)}$$

$$\underline{V_{PE}^{diss}} = \frac{S_{PE}^{diss}}{\rho_{PE}^{am}(T)} m_{solvent}$$

Where S_{PE}^{diss} is the mass of dissolved polymer per gram of diluent used during the swelling experiment, and $\rho_{PE}^{am}(T)$ is the amorphous density of the polymer corrected for the thermal expansion.

The corrected swelling for polymer dissolution in diluents and polymer thermal expansion is given by:

$$\underline{SW_{corr}(\%)} = \frac{V_{PE,corr} - V_{PE,corr}^i}{V_{PE,corr}^i} \times 100$$

It is important to note that the maximum temperature in each experiment varies as a function of the type of diluent. For heavier diluents, temperature steps were performed up to 100°C for the swelling experiments. As will be seen below, some of the lighter diluents (i.e. n-butane, n-pentane, n-hexane) can strongly plasticize the polymer at lower temperatures, and can cause the particles to lose their integrity; the maximum temperature achieved was around 80°C.

2.4.2. Disc Swelling Experiments

As a check on the bulk swelling technique a limited number of swelling experiments were carried out using pressed discs of HDPE-B and LLDPE-I. The polymer was placed in the press, which was heated to 190°C for 1.5 hours. The resulting discs weighed approximately 1.5 g (the exact weight was determined prior to each experiment), and had a diameter of approximately 2.5 cm and a height of 0.25 cm (as with the disc mass, these dimensions are precisely recorded for each disc before each experiment). The edges of the discs were smoothed before being weighed; the smoothing facilitates the optical measurement of swelling. Note that it is necessary to fully melt the powders in the press. Attempts were made to make discs simply by applying pressure to the reactor powder at temperatures just below their melting points. While it is possible to make discs in this manner, said discs lost their cohesion and disintegrated during the swelling experiments. One might suspect that the melting and recrystallization of the powders could influence the swelling, but as we will see below this does not appear to be the case for the limited number of experiments that were run.

Each disc was placed on a metallic support in a transparent 125 mL jacketed glass reactor. Water was circulated through the jacket using a thermostatted bath to control the swelling temperature. 2 Celestron MicroDirect 1080p HD Handheld Digital Micro Viewing Digital Microscopes were positioned around the reactor, one in the plane of the disc to measure vertical swelling, and the other directly above the sample to control changes in the diameter. Care was taken to ensure that the microscopes were well-aligned with the discs in each direction.

The discs were then removed, the reactor filled with 50 mL of n-hexane and the contents were heated to the desired temperature. Once the measurement temperature was reached in the reactor, the discs were replaced, the alignment re-validated, and images of the swelling were sent from the microscopes to a computer for storage and treatment. Several runs were conducted at 60° and 70°C until no change in volume was observed for 1 hour. At this point it was assumed that we have arrived at the equilibrium swelling. The measurement was repeated 5 times for each experimental condition, and the swelling was reported as the average value of these 5 runs. The relative amount of swelling was determined in the same manner as in the bulk powder experiments described above (correction of the final volume for polymer dissolution and thermal expansion).

3 Results and Discussion

3.1 Polymer solubility in alkanes

To properly interpret the sorption and swelling experiments presented in the next sections, it is necessary first to know how much polymer can dissolve into the continuous phase during the experiments. This is done by developing a temperature dependent correlation of the mass of polymer dissolved with respect to the mass of diluent used during the swelling experiments. The percentage of the polymer dissolved as a function of temperature can be seen in Figure 1, and the resulting correlations are given in Table 2.

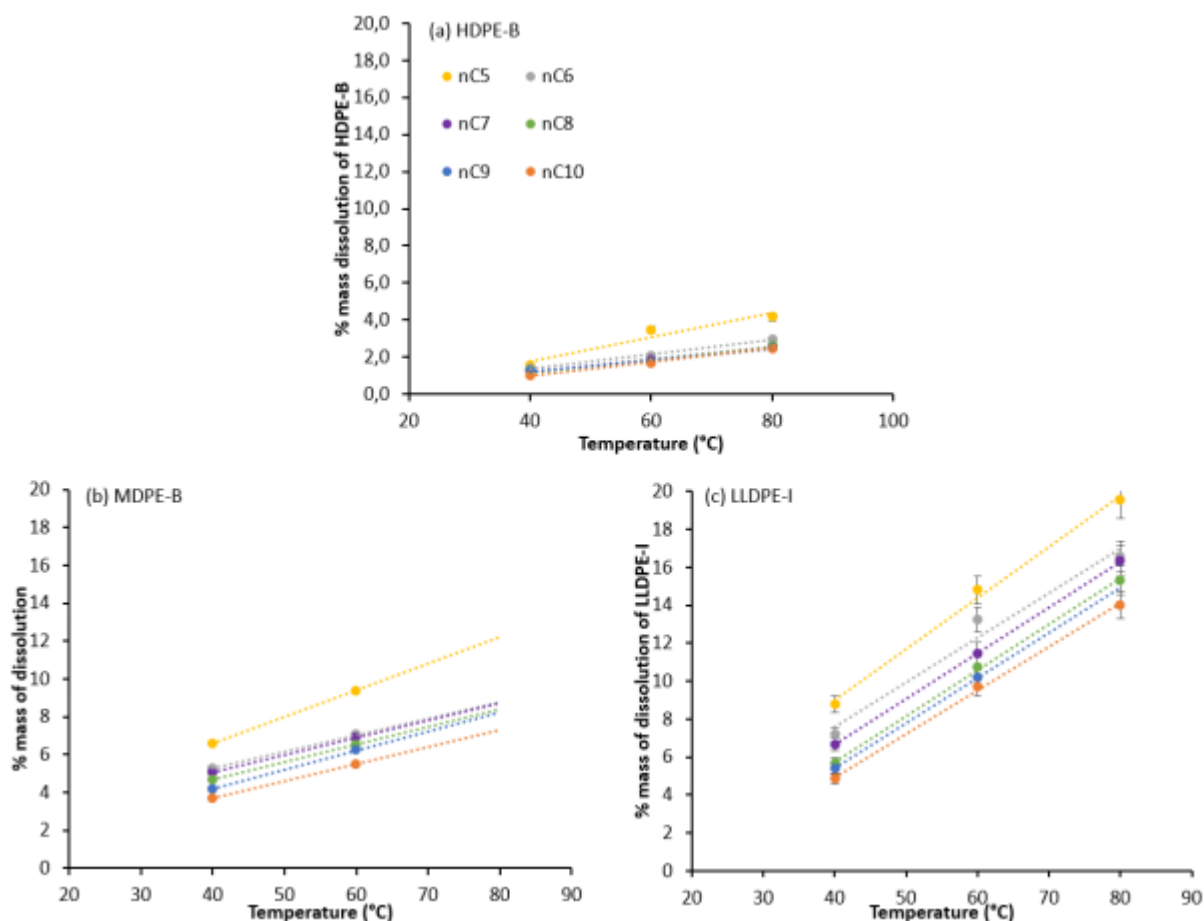


Figure 1. Percent mass dissolved of (a) HDPE-B, (b) MDPE-B, and (c) LLDPE-I powders in the presence of different diluents and at different temperatures.

Table 2. Temperature dependence correlation for the mass of dissolution of PE powders in different diluents (nC₅, nC₆, nC₇, nC₈, nC₉, nC₁₀ signify normal pentane, hexane, heptane, octane, nonane and decane respectively)

Diluents	HDPE-B	MDPE-B	LLDPE-I
nC ₁₀	$\frac{\% \text{diss}}{\text{mass}} = 0.0374 \times T - 0.52$	$\frac{\% \text{diss}}{\text{mass}} = 0.0893 \times T + 0.13$	$\frac{\% \text{diss}}{\text{mass}} = 0.229 \times T - 4.24$
nC ₉	$\frac{\% \text{diss}}{\text{mass}} = 0.0317 \times T - 0.0$	$\frac{\% \text{diss}}{\text{mass}} = 0.1012 \times T + 0.16$	$\frac{\% \text{diss}}{\text{mass}} = 0.239 \times T - 4.16$
nC ₈	$\frac{\% \text{diss}}{\text{mass}} = 0.0347 \times T - 0.2$	$\frac{\% \text{diss}}{\text{mass}} = 0.0919 \times T + 1.0$	$\frac{\% \text{diss}}{\text{mass}} = 0.241 \times T - 3.91$
nC ₇	$\frac{\% \text{diss}}{\text{mass}} = 0.0333 \times T - 0.10$	$\frac{\% \text{diss}}{\text{mass}} = 0.0909 \times T + 1.44$	$\frac{\% \text{diss}}{\text{mass}} = 0.241 \times T - 3$
nC ₆	$\frac{\% \text{diss}}{\text{mass}} = 0.0386 \times T - 0.17$	$\frac{\% \text{diss}}{\text{mass}} = 0.0875 \times T + 1.80$	$\frac{\% \text{diss}}{\text{mass}} = 0.235 \times T - 1.80$
nC ₅	$\frac{\% \text{diss}}{\text{mass}} = 0.065 \times T - 0.838$	$\frac{\% \text{diss}}{\text{mass}} = 0.14 \times T + 0.989$	$\frac{\% \text{diss}}{\text{mass}} = 0.269 \times T - 1.78$

These results show that, as expected, the polymer dissolution increases with increasing the temperature from 40 to 80°C, and with lighter diluents. nC₅ dissolves more polymer per gram than does nC₁₀ for all types of polyethylene. Additionally, the amount of polymer dissolved in the different diluents depends on the polymer type, with more crystalline polymers (i.e. HDPE) dissolving much less than more amorphous products. These results also demonstrate that correcting for dissolution is important as up to 20% of the polymer can dissolve in a diluent at temperatures approaching 80°C.

3.2 Alkane sorption in polymers – Room Temperature Experiments

The solubility of n-pentane, n-hexane, n-heptane, n-octane, n-nonane and n-decane in PE pellets (i.e. HDPE-I) and films (i.e. HDPE-B, MDPE-B, LLDPE-I) was first measured at room temperature. The desorption time was constant for each granule and film in order to have reproducible results. Each desorption experiment was repeated at least 3 times under the same conditions. Figure 2 shows the repeatability of the sorption of nC₆ in HDPE-I, with a difference at time zero of the desorption curve (this is in fact the solubility) of 1.2% between each sorption experiment in presence of n-hexane in HDPE-I granules. The solubility (average of all repeated runs) of each alkane in the different polymers is shown in Table 3.

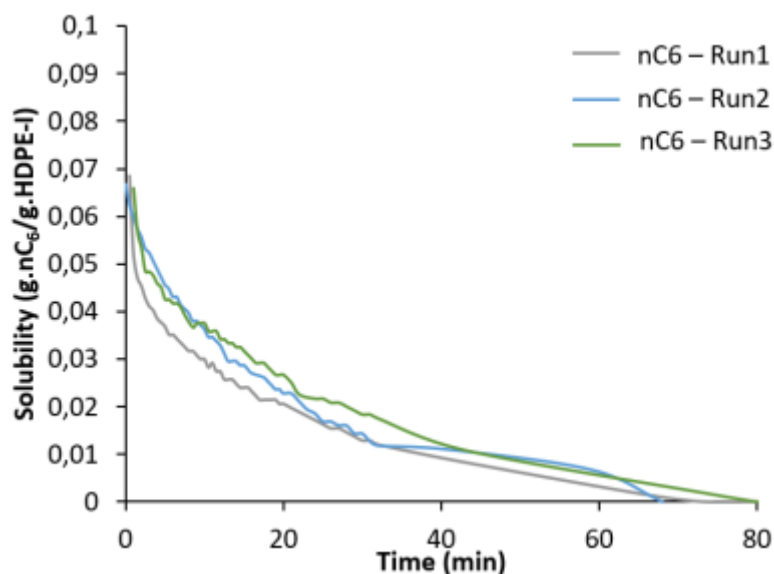


Figure 2. Solubility of n-hexane in HDPE-I granules at room temperature (the same experiment at the same conditions was repeated three times).

Table 3. Comparison of the solubility of different liquid diluents in all PE samples

	HDPE-I (granule)	HDPE-B (film)	MDPE-B (film)	LLDPE-I (film)
nC₅	0.069	0.071	0.075	0.087
nC₆	0.067	0.069	0.072	0.078
nC₇	0.063	0.062	0.066	0.069
nC₈	0.059	0.06	0.061	0.065
nC₉	0.049	0.05		
nC₁₀	0.044	0.047	0.034	0.037

It can be seen from the results in Table 3 that increasing the diluent chain length decreases its solubility in the polymer. The difference of solubility between the heavier (i.e. n-decane) and the lighter (i.e. n-pentane) diluent in HDPE-B and HDPE-I is about 54%. Figure 3 shows the solubility of n-pentane, n-hexane, n-heptane and n-octane in different polyethylene samples as a function of the polymer density. It is interesting to note that the observed solubility with respect to total sample weight (Figure 3(a)) shows only a very slight decrease of solubility as a function of the density. However, when the solubilities are reported as a function of the weight

of the amorphous fraction of the polymer (Figure 3(b)), the trend is reversed. If one focuses on the range of densities from 925 to 970 kg m⁻³, these tendencies are very similar to the solubility results reported by Krajakova et al.^[33] who studied the solubility of n-hexane in different polyethylene samples of densities from 900 to 970 kg m⁻³.

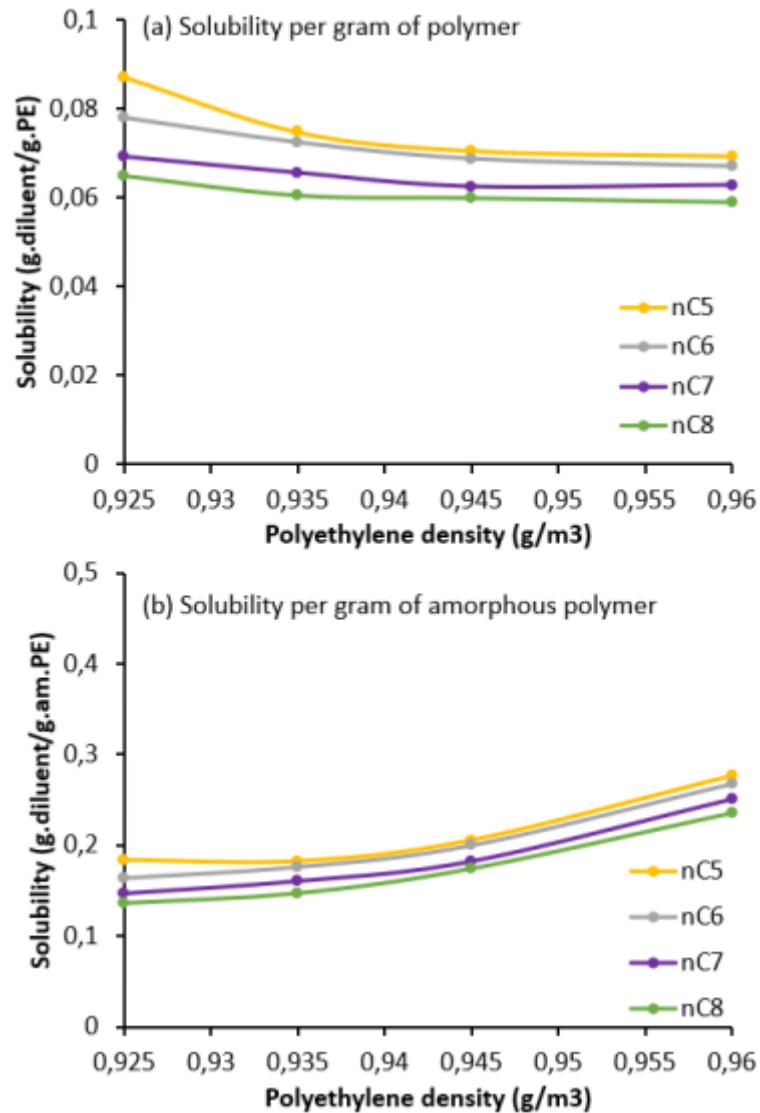


Figure 3. Solubility of different diluents (a) per gram of polymer and (b) per gram of amorphous polymer at room temperature of the different diluents in three different PE samples having different densities.

3.3 Alkane sorption in polymers – TGA Method

Figure 4 shows the solubility of different diluents (nC₅, nC₆, nC₇, nC₈, nC₉, nC₁₀) in HDPE-I granules at different temperatures (25, 40, 60 °C) as measured with the TGA method.

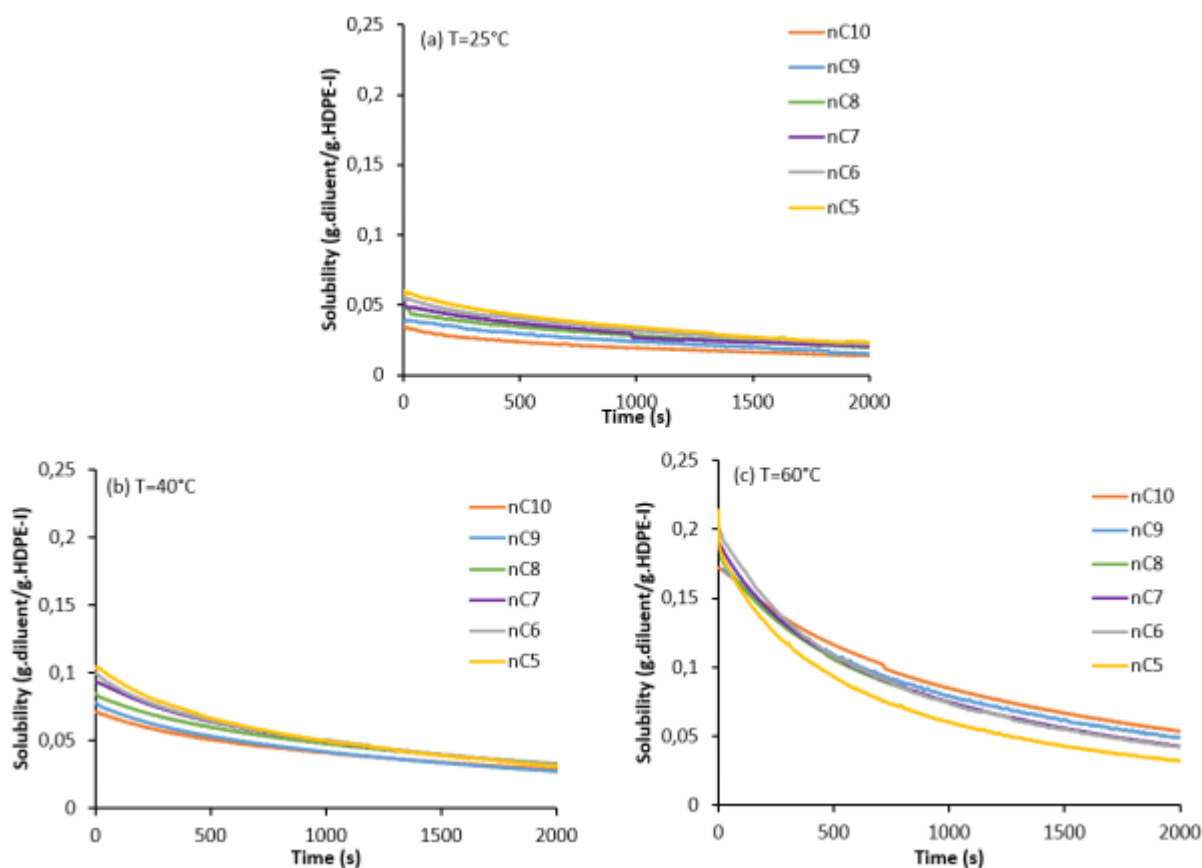


Figure 4. Solubility of different diluents (nC5, nC6, nC7, nC8, nC9, nC10) in HDPE-I granules at 25°C (Each experiment was repeated at least two times under the same conditions)

It can be seen here that, as expected, solubility increases with increasing the temperature and with decreasing the number of carbons of the penetrant. The enhancement of the solubility of lighter diluents (i.e. n-pentane, n-hexane, n-heptane) is more important at higher temperatures than it is with heavier diluents. However, as we will see below, the increase of the solubility of light diluents at high temperature can cause the polymer to swell considerably with these same liquids.

3.4 Swelling experiments

Swelling experiments were run with different diluents (nC4, nC5, nC6, nC7, nC8, nC9, nC10) at temperatures between 30-100°C. All the experiments were carried out at least two times at the same conditions (temperature, identical agitation, and PE powders), and the results shown are an average of the repeated runs. It is important to note that the swelling of PE in presence of n-butane has not been corrected for the partial dissolution of the polymer in the solvent as the experimental procedure presented above is not appropriate for gases. For this reason, the

swelling experiments in presence of n-butane were not performed at high temperature where the dissolution of the polymer is supposed to be significant, and used only HDPE powders.

Before presenting the set of results for the 3 different polymers used in the current study, it is useful to show how important it can be to take into consideration the dissolution of the polymer in the continuous phase in certain cases (i.e. why we need the results presented above). The swelling measured directly from the experimental set-up and the swelling calculated after correction for the mass of dissolved LLDPE-I (c.f. Table 2) as shown in Figure 5. It can be seen that there are noticeable differences in the temperature dependence of the swelling with, and without the correction, especially at higher temperatures where polymer dissolution is non-negligible.

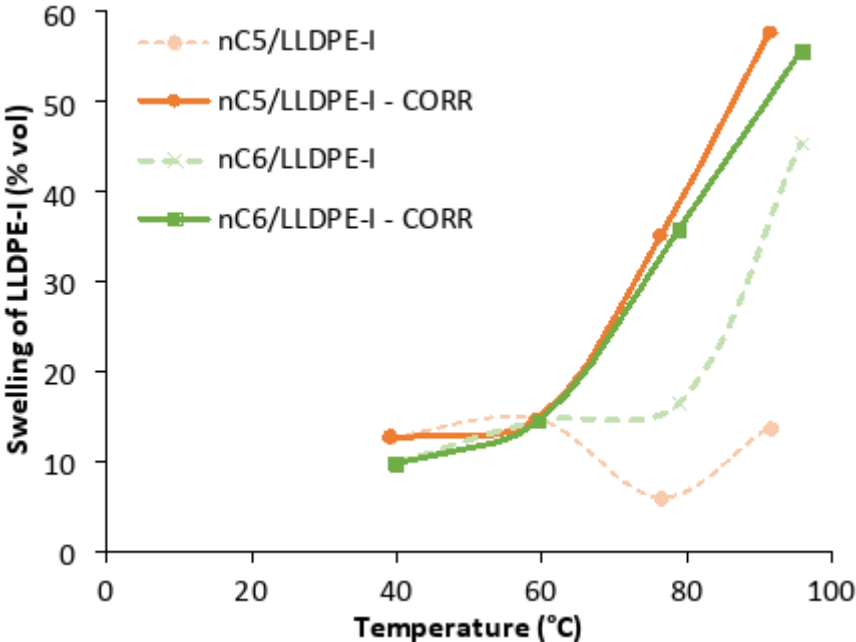


Figure 5. Experimental swelling of LLDPE-I in n-pentane and n-hexane. Raw data (dashed lines) and data corrected for polymer loss due to swelling (solid lines).

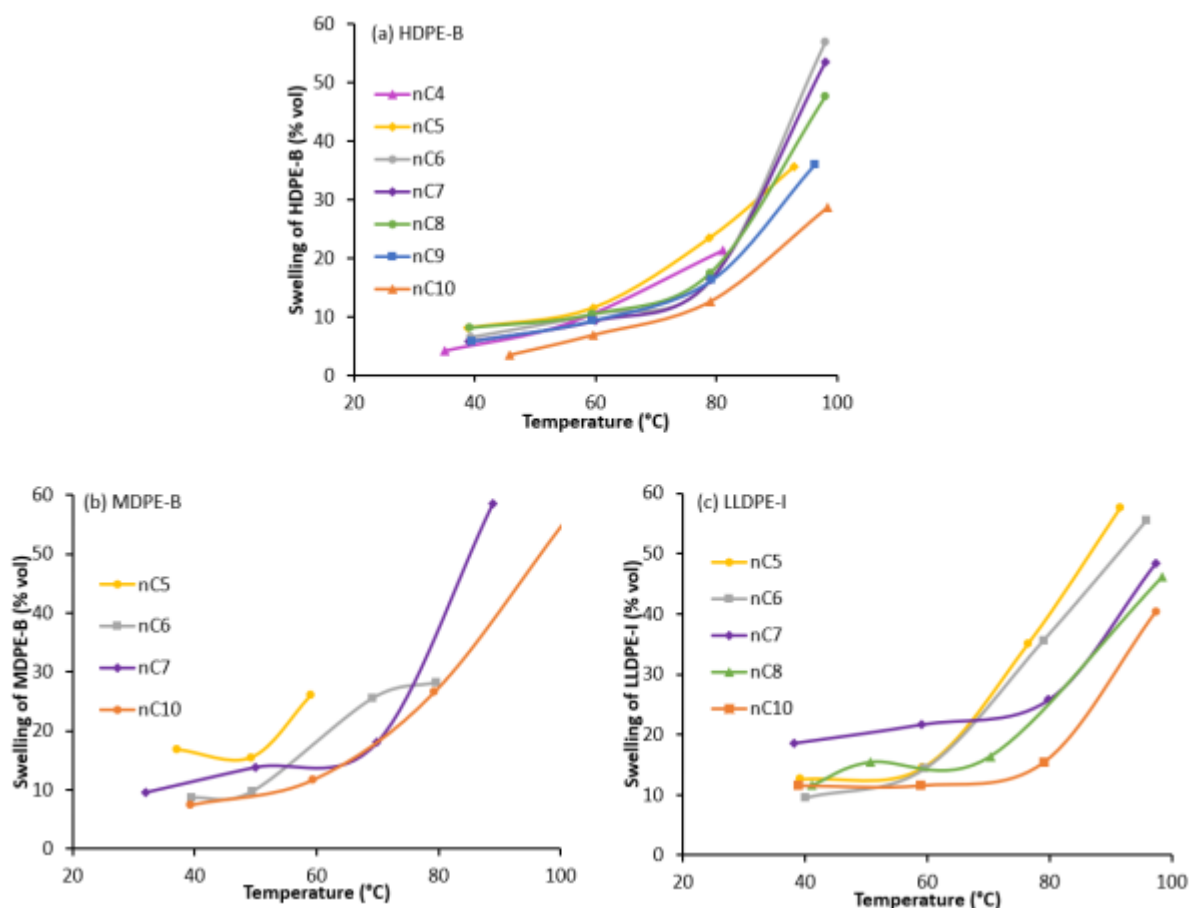


Figure 6. Swelling (in % volume, corrected for dissolution) of (a) of HDPE-B, (b) MDPE-B, and (c) LLDPE-I powders in presence of different diluents at different temperatures.

Figure 6(a) shows that the swelling of HDPE-B is constant at 5-9% for the diluents considered here and at temperatures below 70°C. Starting at, or slightly before 70°C, the swelling begins to increase rapidly. The point where the swelling starts to change rapidly with temperature is often referred to as the breakthrough point (and these curves are sometimes called breakthrough curves). There is some scatter in the data, but it is possible that the increase in swelling is less significant for heavier alkanes than lighter ones, which would be coherent with the solubility results presented above. Similar trends can be seen for the other 2 polymers. The greatest differences in swelling are seen for the lighter diluents where the breakthrough points occurred at lower temperatures for MDPE-B (Figure 6(b)) and LLDPE-I (Figure 6(c)). For MDPE-B and LLDPE-I it was necessary to stop the experiments around 60°C for n-pentane and 80°C for n-hexane because the powders begin to form a gel, such as the one shown in Figure 7. Unlike the swelling of polymers by an alkane which is reversible, the formation of these gels was not (at least on a time frame of a day). Once removed from the reactor, these gels retained their size

and form. While this mixture is not a gel in the sense that the polymer molecules are not cross-linked, they clearly form a 3 dimensional structure that irreversibly traps the diluent molecules.



Figure 7. Example of plasticization/gelation of MDPE-B powders in presence of n-hexane at 90°C.

Finally, as a check on the results of the bulk powder swelling experiments, 4 disc swelling experiments were run and the results are presented in Figure 8. These results are useful for several reasons. One can see that the calculated values for polymer swelling at 60°C and 70°C are very close for the 2 very different techniques. The fact that the results of the two different experimental approaches are so similar implies that swelling of the bulk powder does not appear to have a significant impact on the packing factors of the powders considered here (however, one should be careful about extrapolating these results to other powders with different morphologies). Finally, it also appears that the melting/recrystallization of these specific powders does not influence their swelling in the range of 60°-70°C. Note that since we are obliged to leave the lid off the reactor to control the expansion of the disc in different directions, it is not practical to run the disc swelling experiments at higher temperature or with solvents lighter than hexane. So, while the limited number of experiments presented in Figure

8 allow us to have confidence in the bulk powder swelling experiments, one cannot draw conclusions from the disc swelling experiments outside of the range of conditions examined here.

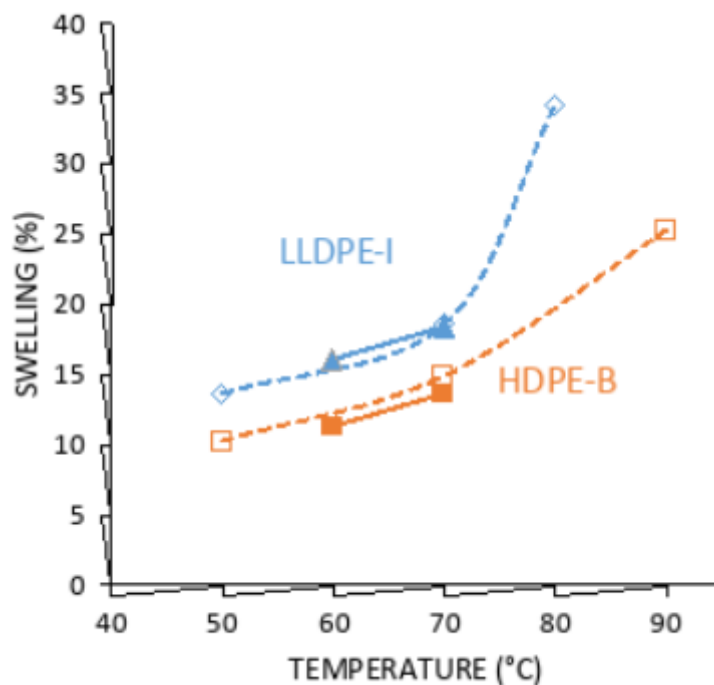


Figure 8. Comparison of disc and bulk powder swelling experiments. Dotted lines are the bulk powder swelling and the solid lines and points are the results of the disc swelling experiments.

4 Conclusion

The sorption of liquid diluents in PE samples as well as the swelling and the dissolution of PE samples was studied in this paper. Indeed, a profound lack of data concerning phase equilibria for PE/liquid diluent systems can be found in the open literature. The thermodynamic of liquid diluents in PE samples was therefore studied at relevant industrial conditions; temperatures up to 100°C and isobutane to n-decane as liquid diluents.

It is shown that the smaller the alkane is, the higher its mass solubility in the amorphous phase of a given polymer is, the greater the solubility (g/g) of polymer with a given density is, and the more the alkane swells a polymer at a given temperature. As expected, polymers of lower density swelled and dissolved more in each alkane. Furthermore, it was also shown that increasing the temperature increases the solubility of the different liquid diluents in the amorphous phase of the polymer.

At temperatures below 60 (LLDPE)-70°C (HDPE), the degree of swelling appears to be more or less constant for all types of polymer, and then increases significantly as the temperature increases, leading to reactor fouling by polymer adhesion and eventually the formation of gels where the diluent is irreversibly trapped in the swollen polymer matrix. This transition from a reversibly swollen linear polymer to an irreversible gel-like structure occurs at temperatures as low as 60°C for LLDPE and light alkanes such as iso-butane or n-pentane. This drastic increase of swelling is a very important property that needs to be controlled in industrial reactors, and is therefore crucial for optimizing reactor operation, as well as in constructing realistic reactor models.

The next logical steps in better understanding the swelling of polymers in alkane solutions will include a more in-depth study of the impact of the molecular weight distribution on the interaction between alkanes and polymer, as well as to include the effect of monomer pressure on the swelling behaviour.

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