Sorption of contaminants into thermoplastic pipes: A Critical Review

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Abstract. For several decades, polymeric materials have been increasingly used in various fields, particularly in the distribution of drinking water thanks to the various advantages represented by polymers such as light weight, low cost, ease of installation and without any problem of corrosion compared to metal pipes. One of the main concerns of researchers is the sorption of the constituents of drinking water through the pipe. Many studies have found that the mass transfer of a liquid into the polymer has consequences such as the change of crystallinity, the yellowing of the polymer, decrease of mechanical resistance and the swelling of the polymer. The aim of this study is to carry out a review about the sorption of the constituents of liquid transported into the material in order to summarize what is already done in this field. We started with the theoretical study of sorption then the experimental one by showing the different methods used to measure the diffusivity of a contaminant towards the polymer then we enumerated the empirical and analytical models developed for predicting diffusivity and solubility coefficients and finally we showed the influence of this transfer on the mechanical characteristics and the morphology of thermoplastic pipes.

1. Introduction

For several decades, polymer materials have seen their use increase in various fields, particularly in the distribution of drinking water in pipes or fittings. Polyethylene and PVC are the most commonly used materials for the transport of drinking water in Morocco thanks to the various advantages they offer such as lightness, low cost, ease of installation and the absence of corrosion problems compared to metal pipes.

If the soil and water environment are contaminated then the buried water pipes will come into contact with the pollutants and despite the fact that plastics are said to be impermeable to chemicals but the molecules of some products can penetrate. Therefore, understanding the sorption of contaminants in the pipe is now a requirement to assess the future use of the distribution system.

The sorption process begins with an adsorption of the molecules that settle on the inner surface of the pipe and then an absorption of these molecules into the pipe which is managed by the partition coefficient $K$ and finally diffusion of sorbed contaminant molecules through the amorphous area within pipe materials.

Several factors influence this mass transfer, including environmental conditions, pipe properties and contaminant properties. Contaminants diffuse into the amorphous regions of the material, the cross-linking, the bulk density of the pipe, the size shape and polarity of the contaminants can also influence polymer interactions[1].

In this study, a review of available literature was developed about the sorption of contaminants into thermoplastic pipes in order to serve as a source of background information and to summarize what is already done in this topic area. The specific objectives of this study were: 1-initializing the theoretical
study of sorption 2- listing the different methods used to measure the diffusivity of a contaminant towards the polymer 3- identifying the empirical and analytical models developed for predicting diffusivity and solubility coefficients and finally we showed the influence of this transfer on the mechanical characteristics and the morphology of thermoplastic pipes.

2. Theory

The background between the pipe and the drinking water is a heterogeneous background so diffusion is controlled by fick’s law:

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}
\]  

(1)

The solution of this equation for the case of diffusion in polymers is given by Crank and Park [2] using the following assumptions:

The diffusion coefficient \( D \) is constant (does not depend on the concentration)

Initial conditions : \( t=0 ; C(x)=f(x)=0 \)

Boundary conditions: \( t>0; C(x=0)=C_1 = C_\infty \)
\( C(x=L)=C_2= C_\infty \)

\[
\frac{C(t,x)}{C_\infty} = 1 - 4 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left( -\frac{D(2n+1)^2\pi^2}{l^2}t \right) \sin \left( \frac{(2n+1)\pi}{l}x \right)
\]

(2)

We have \( M_t = \int_0^l C(t,x)dx \)

So the simplified formula for diffusion in polymers is:

\[
\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{\pi^2(2n+1)^2} \exp \left( -\frac{D(2n+1)^2\pi^2}{l^2}t \right)
\]

(4)

To determine the diffusion of a contaminant in a thermoplastic tube, a parameter is calculated which is the diffusivity and is estimated by calculating the slope of the curve \( \alpha \) drawn from the equation (5)

\[
\frac{M_t}{M_\infty} = f\left( \sqrt{t} \right) \quad \text{(5)}
\]

\[
D = \pi \left( \frac{l \alpha}{4} \right)^2 \quad \text{(6)}
\]

Solubility is also a parameter that allows us to define the ability of a solute to dissolve in a polymer and is calculated according to the following formula:

\[
S = \frac{M_\infty - M_t}{M_t=0} \rho \text{polymère}
\]

(7)

With \( M_\infty \) is the mass of the contaminant in the saturated polymer, \( M_0 \) is the initial mass of the contaminant in the polymer which is equal to 0 and \( M_t=0 \) is the mass of the polymer, \( \rho \) is the bulk density.

3. Methods for measuring diffusivity

In the literature, several experimental techniques are used to study transport phenomena or more precisely the estimation of penetrant diffusivity in polymers like nuclear magnetic resonance (NMR), laser interferometry, gravimetric method and Fourier transform infrared spectroscopy (FTIR).
Britton et al. [3] studied the diffusion and permeability of pollutants through HDPE using the gravimetric method. Scherillo et al. [4] studied water diffusion in PEEK and PEI using the gravimetric method and FTIR by comparing the two. Moylan et al. [5] used a quartz crystal microbalance to study the solubility of water vapour in four different polyimides at 100% relative humidity and 22°C and Kumar et al. [6] studied the sorption and desorption of aromatic molecules in PU and PMMA.

The nuclear magnetic resonance technique has also been used to study polymer/solvent transfer such as toluene in polystyrene, water in nylon, water in glass-filled polyesters, polyvinyl acetate glues in wood, 1,4 dioxane in a polybutadiene elastomer and several organic solvents in PMMA. [7][8][9][10]

Laser interferometry was used by Saenger [11] and Durning et al to study the diffusion of methanol and n-methyl-2-pyrrolidone in polymethyl methacrylate (PMMA). [12]

Fourier transform infrared spectroscopy has also been widely studied. Safa et al. [13] have used it extensively in their work to study ester sorption kinetics in polypropylene films or bottles. Riquet et al. [14] used it to study the sorption of olive oil in polypropylene and determine the concentration profiles in the film thickness. Cava et al. [15] used it to determine the diffusion of flavours through an extruded PolyEthylene film. Cotugno et al. [16] also adapted this approach for the study of water/epoxy systems and finally Ichikawa et al. [17] used this spectroscopic technique to study water sorption in different polymer films.

The two methods most used and recommended by scientists are the gravimetric method and Fourier Transform Infrared Spectrometry (FTIR).

3.1. The gravimetric method:

The gravimetric method is one of the most widely used methods for studying the sorption of a liquid in a solid material, which consists in monitoring the evolution of the mass of a sample immersed in this medium. There are two types of gravimetry measurement: static and dynamic methods.

The protocol consists first of all in preparing the samples in advance, then in putting them in contact with the chosen solution. Over time, the sample is removed, wiped, dried and weighed using a microbalance to calculate the difference in mass before and after contact [18].

The collected measurements make it possible to draw a curve equation (5) and thus to find the diffusivity D which represents the slope of the curve.

Figure 1 above shows an example of sorption kinetics of amyl acetate sorption in polypropylene at different concentrations at T=23°C.
3.2. The FTIR method

Fourier Transform Infrared Spectroscopy (FTIR) is based on the absorption of infrared radiation by the analyzed material. It allows, through the detection of the characteristic vibrations of the chemical bonds, to carry out the analysis of the chemical functions present in the material. Infrared spectrometry is the measurement of the decrease in the intensity of radiation passing through a sample as a function of wavelength. This intensity measurement at each wavelength leads to a spectrum characteristic of the product under study.

The spectrum obtained represents \( I/I_0 = f(\tau) \) with \( I \): absorbed intensity, \( I_0 \): initial intensity and \( \tau = 1/\lambda \).

\[
\frac{A_r}{A_\infty} = f(\sqrt{t}) \quad (8)
\]

\[
A_r = \frac{A_t}{A_{pp}} \quad (9) \quad \text{With } A_t \text{ is the peak absorbance area of amyl acetate at time } t \text{ and } A_{pp} \text{ is the area of the characteristic peak absorbance of polypropylene.}
\]

\( A_\infty \) is the ratio of areas to equilibrium.

![Figure 2: virgin polypropylene spectrum, [18]](image1)

![Figure 3: spectrum of polypropylene in contact with amyl acetate at T=23°C, [18]](image2)

To quantify the absorbed product, the ratio of the areas \( A_r \) of absorbance at time \( t \) is plotted on \( A_\infty \) as a function of the square root of the ageing time:

![Figure 4: evolution of area ratios during sorption of amyl acetate in polypropylene, [18]](image3)
The diffusion coefficient is obtained by calculating the slope of the linear part of the curve. FTIR offers the possibility to simultaneously measure the permeability of various penetrants and through the analysis of band shape changes and band shift it is possible to evaluate the different types of interactions that can be established between the polymer and the penetrant at different sorption stages. Thanks to FTIR, sorption can also be easily and accurately evaluated through very thin films [15].

4. Empirical and analytical models:

Several authors have studied the sorption of contaminants through thermoplastic pipes used for the transport of drinking water. Before outlining the models developed by these authors, we will first identify the types of contaminants and the thermoplastic pipes used to do so.

4.1. Contaminants:
The selected contaminants are components commonly found in contaminated hazardous sites and the selection are based on their frequency of detection in contaminated environments [19][20] Tang et al.[1] assumed that some important properties of contaminants influence polymer interactions like polarity µ , molar volume Mv , molecular weight Mw , water solubility Sw , the density of contaminant ρc and the log form of octanol water partition coefficient logKow..

The table below give the properties of the 14 contaminants selected:

| Contaminant      | µ debye | Mv cm³/mol | Mw g/mol | Sw (%) | ρc g/cm³ | logKow |
|------------------|---------|------------|----------|--------|----------|--------|
| Acetonitrile     | 3.92    | 53.5       | 41.05    | 100    | 0.786    | -0.34  |
| Benzaldehyde     | 2.80    | 120.5      | 106.12   | 0.3    | 1.041    | 1.48   |
| Benzyl alcohol   | 1.71    | 125.1      | 108.14   | 4.0    | 1.041    | 1.10   |
| 1-butanol        | 1.66    | 96.2       | 74.12    | 7.4    | 0.809    | -0.30  |
| 2-butanol        | 2.76    | 91.4       | 72.11    | 22.3   | 0.805    | 0.29   |
| 1,2-dichloromethane | 1.9 | 79.01      | 98.96    | 0.87   | 1.25     | 1.45   |
| Dichloromethane  | 1.14    | 60.6       | 84.93    | 1.303  | 1.326    | 1.25   |
| MTBE             | 1.36    | 119.1      | 88.15    | 5.1    | 0.740    | 1.24   |
| 2-propanol       | 1.56    | 77.8       | 60.10    | 100    | 0.789    | 0.05   |
| 2-propanone      | 2.88    | 73.1       | 58.08    | 100    | 0.789    | -0.24  |
| Trichloromethane | 1.01    | 74.4       | 119.37   | 0.729  | 1.492    | 1.97   |
| Toluene          | 0.36    | 117.7      | 92.14    | 0.0526 | 0.867    | 2.73   |
| m-Xy廉洁         | 0.30    | 135.9      | 106.16   | 0.0161 | 0.864    | 3.20   |
| p-Xy廉洁         | 0.00    | 135.8      | 106.16   | 0.0162 | 0.867    | 3.15   |

4.2. Types of thermoplastic pipes:
PVC pipe: PVC is an amorphous thermoplastic with a glass transition temperature (Tg) of 82°C. Because its Tg is higher than the ambient temperature, PVC is a glassy and rigid plastic.[21] At present, there are three types of PVC pipes used in Morocco: unplasticized PVC-U used for drinking water, overchlorinated PVC-C used for the installation of cold and hot water and bioriented PVC.
PE pipe: There are many types of PE pipes with different chemical composition and operating conditions, but these materials have always been classified as PE. All PE pipes have a Tg below zero,
so the material is flexible at room temperature and below ground temperature. All PE pipes are manufactured from PE resins with different densities, crystallinities and Tg values:

Low density:
- **PELD** \(0.910 \text{ g/cm}^3 < \rho < 0.925 \text{ g/cm}^3\), \(T_g = -20 ^\circ\text{C}\)

Medium density:
- **PEMD** \(0.926 \text{ g/cm}^3 < \rho < 0.940 \text{ g/cm}^3\), \(T_g = -70 ^\circ\text{C}\)

High density:
- **PEHD** \(\rho \geq 0.941 \text{ g/cm}^3\), \(T_g = -140 ^\circ\text{C}\)

**PPR pipe:**
Random polypropylene (PP-R) is a widely used material for pipe applications. To protect the polymer against oxidative degradation during service, it is stabilised with phenolic antioxidants. Polypropylene is a semi-crystalline thermoplastic that is semi-rigid and highly resistant to abrasion with a \(T_g\) equal to \(-10 ^\circ\text{C}\) and a density 0.9 g/cm3.

### 4.3. Model of Aminabhavi 1999:
Aminabhavi et al. [22] studied the sorption, desorption and permeability of contaminants through HDPE geomembranes using the gravimetric method using the following formula:

\[
C_t = \frac{W_t - W_0}{W_0} \times \frac{1}{M}
\]

With \(W_t\) is the mass at \(t\), \(W_0\) the initial mass of the sample and \(M\) the molar mass of the solvent and thanks to these experimental data he developed an expression of these three parameters based on Arrhenius’ law which takes into consideration the effect of temperature.

\[
X = X_0 \times e^{-\frac{E_x}{RT}}
\]

With \(E_x\) is the activation energy that has been obtained by the least squares procedure.

### 4.4. Model of chao2007:
Chao et al. [23] determined the diffusion and solubility coefficients of organic solvents through HDPE geomembranes using 2 methods: the ASTM F739 permeation experiment and the immersion experiment, after which he proceeded with numerical analysis to solve the one-dimensional fick equation:

\[
C_z(z, t) = kC_f(1 - \frac{Z}{L} - \sum_{n=1}^{\infty} \frac{2}{n\pi} \exp \left( -\frac{Dt (nn)^2}{l^2} \right) \sin \left( \frac{n\pi}{l} z \right))
\]

Based on the following conditions:
- \(C(0)=S=KC_f\)
- \(C(l)=0\)
- \(t=0, C_z=0\)

Where \(K\) is the solubility coefficient and the \(C_f\) is the equilibrium concentration of the permeate.

The initial conditions are the data we had experimentally.

The simulation showed that the immersion method is inappropriate and that ASTM F739 describes better the boundary conditions.

### 4.5. Model of Tang 2013:
Tang et al. [1] predicted the solubility and diffusion coefficients of contaminants through HDPE. His model was based on the properties of the contaminants and the pipe. The regression method was adopted to select the variables and the linear multiple regression was used to develop the equations. The model was based on experimental data found by Whelton et al. [24].
The validation of the model was done by comparing the results of the model with experimental data from the literature.

The model is as follows:
Diffusivity = 103.10 - 0.840µ - 0.085 Mv + 2.263logKow - 98.066 ρ
Solubility = 0.6734 - 0.00852µ - 0.00111 Mv + 0.0377 logKow - 0.577 ρ

5. Influence of sorption on the pipe:
The pipes used in water distribution networks are subject to environmental constraints, their lifespan depends a lot on the retention of antioxidants by the material. In dry air, polyethylene can retain its properties for several decades. However, when polyethylene pipes are used in networks and chlorine is present in the water, chlorine can diffuse and penetrate, causing the material to lose its antioxidants.

Several authors have studied the influence of the presence of chlorine in water on the pipe. Dear et al.[25] studied the effect of chlorine on polyethylene pipes in water distribution networks. He found that the lifetime of a pipe is determined by the formation of the brittle layer on the inner surface of the pipe and the formation of this layer is promoted and accelerated in the presence of chlorine in the water because of its diffusion in the pipe, antioxidants are consumed. And this change of physical properties included a reduction of yield stress, elongation to failure, and molecular mass. He has been shown also that because of high chlorine levels the expected 50-years life of HDPE pipes can be reduced and he confirms that if the pipes are located in well-drained soil without containing industrial chemicals the lifespan can be extended more than 50 years.

Whelton et al. [26] have elaborated an accelerated aging with chlorinated water with 45 mg free chlorine for 141 days and found that it had no effect on the surface properties of MDPE-based PEX-A pipes. However, these aging conditions affected the properties of HDPE, HDPE and PEX-B pipes that were aged in the laboratory by the formation of carbonyl bonds on the surface and the significant loss of the oxidative induction time OIT.

6. Conclusion
A review was developed about sorption of contaminants into thermoplastic pipes, we initiate the methods to measure the diffusivity and the models available in the literature and finally their effect on the pipe but we observe that informations and studies about this phenomenon are few and models that take into account the different factors that influence the diffusion of contaminants through the pipes were missing. The study of the influence of this transfer has highlighted just the degradation of the pipe (the OIT) but data concerning the effect of the transfer on the mechanical characteristics of the pipe, on melting and glass transition temperatures and finally on the morphology of the pipe after contact are also missing.

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