

# Mathematical Modelling of Corrosion for Polymers

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**Abstract** The material of pipelines transporting water is usually polymers. Chlorine as oxidant agent is added into the water system to prevent the spread of some disease. However, exposure to a chlorinated environment could lead to polymer pipe degradation and crack formation which ultimately reaches a complete failure for the pipes. To save labor, time and operating cost for predicting a failure time for a polymer pipe, we focus on its modeling and simulation. A current kinetic model for the corrosion process of polymers due to the action of chlorine is extensively analyzed from the mathematical point of view. By using the nondimensionalization method, the number of parameters in the original governing equations of the kinetic model has been reduced. Then, the dimensionless set of differential equations is numerically solved by the Runge Kutta method. There are two sets of simulations which are low chlorine concentration and high chlorine concentration, and we captured some essential characteristics for both types. This approach enables us to obtain better predictive capabilities, hence increasing our understanding of the corrosion process.

**Keywords** Corrosion, Kinetic Model, Mathematical Modelling, Dimensionless

## 1 Introduction

Corrosion on polymers can be obviously seen when there is crack on the polymer surface. However, the corrosion on the polymer is often hard to discover where the material looked normal but internally the strength of the material is weak. In physical testing, it is hard to determine the state of the material and to decide when the maintenance need to take place. To make things worse, sometimes after an accident occurred, then we realized that there is corrosion. To save labor and time, and for the safety purpose, simulation of the corrosion process is necessary to test various conditions and determine the failure time of the pipe. Colin [1] presented a satisfactory prediction of molecular weight loss during the corrosion process. Here in this paper, his kinetic model is extensively studied to analyze the oxidant and antioxidant concentration profiles in polymer pipes.

Deterioration of polymer is one of the main concerns for people working with pipelines industry. A significant effort has been devoted to studying the corrosion due to environmental conditions. Compared with pipes made from other material, the polymer is an anti-corrosion material and low cost compared to metal. Even the polymer is an anti-corrosion material, the exposure to oxidant agent, high pressure and temperature affect the performance of the polymer. The process of polymer corrosion consists of chemical reaction, diffusion, and mechanical deformation. The chronology of corrosion of polymer pipes due to chemical aging is as follows [3]: (a) A polymer is exposed to chlorine (oxidant agent/disinfectants). (b) The antioxidant is added to prevent corrosion. (c) Antioxidant react to the oxidant agent. (d) Antioxidant disappeared slowly (migration). (e) Oxidant absorbs on the polymer surface. (f) Polymer reacts to oxidant directly causing to chain scission and make the molecular chain shorter. Hence, the cause of polymer corrosion is radical chain-oxidation [5].

Polymer pipes that transporting water will undergo failure after a certain time due to the physical and chemical aging. The water contains two reactive species which are oxygen and disinfectants (chlorine dioxide). Disinfectants will destroy organic compounds, often by radical processes. It degraded the inner surface of plastics pipelines, developed cracked and eventually reach a complete failure. The lifetime of a pipeline is normally 50-100 years, however, these factors make the degradation goes faster so that the lifetime becomes shorter i.e. 1-25 years [3].

The complexity of corrosion processes creates the necessity for a quantitative model approach to developing predictive tools, which simultaneously provide both quantitative information as well as simulations of the various processes involved.

The kinetic equations of polymer corrosion have been extensively studied and many kinetic models have been proposed [1][2]. The mechanisms of polymer degradation induced by chlorine dioxide in terms of the kinetic model have been established by [1]. Ge et al. [3] developed a model to investigate the time-dependent crack propagation in a viscoplastic polymer. Their result shows that failure behavior is dependent on the applied load.

The objective of this research is to analyze the oxidant and antioxidant concentration profile in polymer pipes. By analyzing these components, the primary aging process of the pipes

can be understood. We analyzed the problem using a mathematical model developed by in [1].

This paper deals with the effect of chlorine dioxide (DOC) on the aging of polyethylene (PE) pipes for the transport of water. DOC which is a free radical can initiate radical chain oxidation in PE. Oxidation induces random chain scission, and this latter leads to embrittlement when the weight average molar mass  $M_w$  becomes typically lower than 70 kg mol<sup>-1</sup>. A mechanistic scheme for low-temperature PE thermo-oxidation incorporating DOC reactions has been built [1].

In this paper, a nondimensionalization is presented for the governing equations of polymer corrosion kinetic model described in [1]. Using a nondimensionalization of these equations, a number of nondimensional group parameters are proposed. Structurally, this paper consists of thematic sections with relevant subsections. In the first section, we introduce the paper. The second section is concerned solely on the mechanics of the nondimensionalization, where we introduce a mathematical analysis for the model. In the third section, we discuss the solutions. Finally, the conclusion of this paper is provided.

## 2 Mechanics of the Nondimensionalization

The oxidation processes occurring on polymer pipes when exposed to chlorine dioxide. In this section, we aim to introduce a mathematical model able to describe the corrosion effects on a polymer layer, which is subject to deposition of chlorine. The present model is based on the mathematical approach used in [1]. The ten governing equations of the kinetic model for corrosion for polymers were presented in [1].

The complexity of the system makes finding the analytical solution difficult. To solve the system of equations, we perhaps have to resort to numerical methods that can incur significant computational cost. Our strategy here is to look for reduced order models by ignoring significantly small terms in the governing system of equations. The goal is to ensure that mathematical results are consistent with physical requirements.

Reformulating a model in dimensionless form is beneficial from several aspects. This procedure can help to check the consistency of the model equations and confirm that all terms have the same set of units in a differential equation. In addition, nondimensionalizing a model reduces the number of free parameters and reveals a smaller set of quantities that govern the dynamics. Once a model is dimensionless, it shows which terms have a larger or smaller magnitude, which can help to obtain approximate solutions using techniques such as asymptotic analysis. Table 1 represents the unit of each variable.

There are eleven fundamental scales; all others can be derived from these scales. These nondimensional parameters and the scales that they are based upon are:

$$\tau = \frac{t}{t_0}, [doc] = \frac{[DOC]}{C_{in}}, [ah] = \frac{[AH]}{H_{in}}, [o2] = \frac{[O_2]}{G_{in}},$$

$$[ph] = \frac{[PH]}{PH_{in}}, [pooH] = \frac{[POOH]}{POOH_{in}}, [po2] = \frac{[PO_2^*]}{POOH_{in}}$$

Table 1. Parameter units

Parameters	Units
DOC, AH, O <sub>2</sub> , PH, POOH, PO <sub>2</sub> <sup>*</sup> , PO <sub>2</sub> <sup>*</sup>	mol l <sup>-1</sup>
Q, s, x	mol l <sup>-1</sup>
k <sub>1b</sub> , k <sub>1d</sub> , k <sub>1s</sub> , k <sub>s1</sub> , k <sub>2</sub> , k <sub>3</sub> , k <sub>4</sub> , k <sub>5</sub> , k <sub>6a</sub> , k <sub>7</sub>	l mol <sup>-1</sup> s <sup>-1</sup>
k <sub>1u</sub> , k <sub>6b</sub> , k <sub>6c</sub> , k <sub>6d</sub>	s <sup>-1</sup>
n <sub>AH</sub> , γ <sub>1s</sub> , γ <sub>4</sub> , γ <sub>5</sub>	no unit

$$[p] = \frac{[P^*]}{POOH_{in}}, [q] = \frac{[Q]}{POOH_{in}}, \tilde{s} = \frac{s}{s_0}, \tilde{x} = \frac{x}{x_0}$$

where

- $t$  is time,
- $t_0$  is the characteristic time,
- DOC is chlorine dioxide solution,
- $C_{in}$  is initial value of chlorine dioxide solution,
- AH is stabilizer,
- $H_{in}$  is initial value of stabilizer,
- O<sub>2</sub> is oxygen,
- $G_{in}$  is initial value of oxygen,
- PH is polyethylene,
- $PH_{in}$  is initial value of polyethylene,
- POOH is hydroperoxides,
- $POOH_{in}$  is initial value of hydroperoxides,
- PO<sub>2</sub><sup>\*</sup> is radical,
- P<sup>\*</sup> is radical,
- Q is caged pair of PO<sub>2</sub><sup>\*</sup> radical,
- $n_{AH}$  is phenolic stabilizer functionality,
- $s$  is quantity of chain scission,
- $x$  is quantity of crosslinking, and

Therefore, we obtained a dimensionless system as follows.

$$\frac{d[doc]}{d\tau} = -k_{1d}PH_{in}[doc][ph] - n_{AH}k_{1s}H_{in}[doc][ah] - k_7POOH_{in}[doc][p]$$

$$\frac{d[ah]}{d\tau} = -n_{AH}k_{1s}C_{in}[doc][ah] - n_{AH}k_{s1}POOH_{in}[po2][ah]$$

$$\frac{d[o2]}{d\tau} = -k_2POOH_{in}[O_2][p] + k_{6a}POOH_{in}/G_{in}[po2]^2$$

$$\frac{d[ph]}{d\tau} = -(2 + \gamma_{1s})POOH_{in}/PH_{in}k_{1u}[pooH] - (1 + \gamma_{1s})k_{1b}POOH_{in}^2/PH_{in}[pooH]^2 - k_{1d}C_{in}[doc][ph] - k_3POOH_{in}[ph][po2] + 2\gamma_4k_4POOH_{in}^2/PH_{in}[p]^2 + (3\gamma_5 - 1)k_5POOH_{in}^2/PH_{in}[p][po2] + 2k_{6b}POOH_{in}/PH_{in}[q] - 2(1 + \gamma_{1s})k_{6d}POOH_{in}/PH_{in}[q]$$

$$\frac{d[pooH]}{d\tau} = -k_{1u}y(5) - 2k_{1b}POOH_{in}[pooH]^2 + k_3PH_{in}[ph][po2] + (1 - \gamma_5)POOH_{in}[p][po2]$$

$$\frac{d[po2]}{d\tau} = k_{1b}POOH_{in}[pooH]^2 + k_2G_{in}[o2][p] - k_3PH_{in}y(4)[po2] - k_5POOH_{in}[p][po2] - 2k_{6a}POOH_{in}[po2]^2 - n_{AH}k_{s1}H_{in}[po2][ah]$$

**Table 2.** Parameter values for elementary rate constants

Parameters	Value
$\gamma_{1s}$	1
$\gamma_4$	0.5
$\gamma_5$	0.0108
$k_{1b}$	$8.6 \times 10^{-9}$
$k_{1d}$	$2.7 \times 10^{-5}$
$k_{1u}$	$3.6 \times 10^{-11}$
$k_2$	$10^8$
$k_3$	$10^{-2}$
$k_4$	$8 \times 10^{11}$
$k_5$	$1.6 \times 10^{11}$
$k_{6a}$	$2.2 \times 10^6$
$k_{6b}$	$2 \times 10^6$
$k_{6c}$	$1.8 \times 10^5$
$k_{6d}$	$6 \times 10^6$
$k_7$	$2 \times 10^6$
$PH_{in}$	60
$POOH_{in}$	$10^{-2}$
$P_{in}$	0
$PO_2_{in}$	0
$Q_{in}$	0

$$\frac{d[p]}{d\tau} = 2k_{1u}[poo] + k_{1b}POOH_{in}[poo]^2 + k_{1d}C_{in}PH_{in}/POOH_{in}[doc][ph] - k_2G_{in}[o_2][p] + k_3PH_{in}[ph][po_2] - 2k_4POOH_{in}[p]^2 - k_5POOH_{in}[p][po_2] + 2k_{6d}[q] - k_7C_{in}[p][doc]$$

$$\frac{d[q]}{d\tau} = k_{6a}POOH_{in}[po_2]^2 - (k_{6b} + k_{6c} + k_{6d})[q]$$

$$\frac{d[s]}{d\tau} = \gamma_{1s}k_{1u}POOH_{in}[poo] + \gamma_{1s}k_{1b}POOH_{in}^2[poo]^2 + 2\gamma_{1s}k_{6d}POOH_{in}[q]$$

$$\frac{d[x]}{d\tau} = \gamma_4k_4POOH_{in}^2[p]^2 + \gamma_5k_5POOH_{in}^2[p][po_2] + k_{6b}POOH_{in}[q]$$

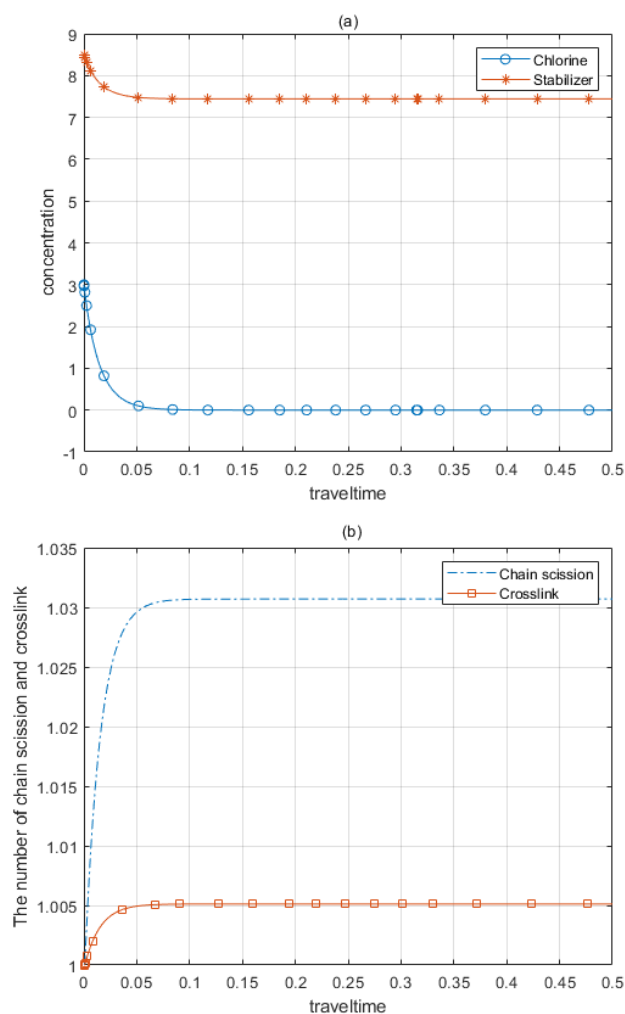
The reduction in the number of parameters makes theoretical manipulation easier, as the equations are less cluttered. We solved the set of dimensionless system of differentiable equations using Runge Kutta method. The parameter values is recorded in Table 2 where we refer [1].

### 3 Results and Discussion

To gain an understanding of the kinetic model, we observe the changes in the behaviour of the system. We fixed the initial concentration of stabiliser and studied how the dynamic change with varying DOC concentration. We assumed the initial concentration of stabiliser is 8.5 mol/l in all simulation study. Elementary rate constants  $\gamma_{1s}, \gamma_4, \gamma_5, k_{1b}, k_{1d}, k_{1u}, k_2, k_3, k_4, k_5, k_{6a}, k_{6b}, k_{6c}, k_{6d}, k_7$  and initial values  $PH_{in}, P_{in}, POOH_{in}$  as recorded in Table 2 have been previously determined in [4] and will be used here without modification. In all simulation, we set

$n_{AH} = 1, k_{1s} = 1, k_{s1} = 1, s_{in} = 1, x_{in} = 1, H_{in} = 8.5$ , and  $G_{in} = 20$ .

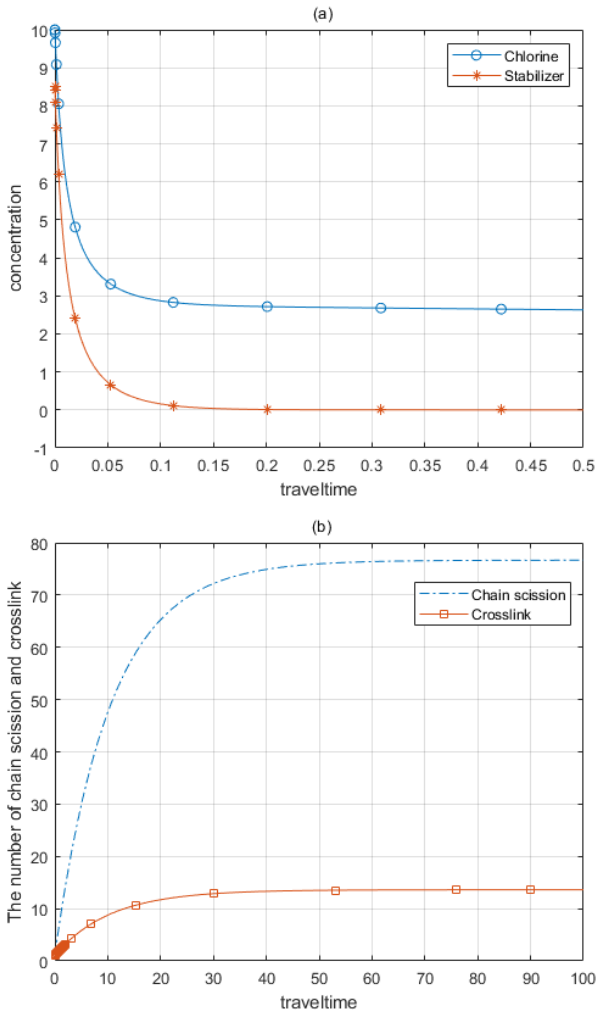
To get insight into the behavior of chlorine and stabilizer, we plot the graphs in Figure 1. In this graph, we set the initial concentration of DOC is 3 mol/l (low DOC concentration). At low DOC concentration, according to Figure 1, the profile of chlorine and stabilizer decreased within a short time and then leveling off. The small amount of chlorine depleted and dropped to zero due to the action of the stabilizer. Chlorine dioxide initiates polymer oxidation. Hence, the numbers of chain scission increased throughout the time before it reached a steady state. The presence of chlorine accelerates the consumption of stabilizers and consequently the degradation of polymer pipes.



**Figure 1.** Low DOC concentration (a) The profile of chlorine and stabiliser concentration (b) The number of chain scission and crosslink when  $H_{in}=8.5$  and  $C_{in}=3$ .

Figure 2 shows the concentration profiles of chlorine and stabilizer at high DOC concentration i.e.  $C_{in} = 10$ . At high DOC concentration, the concentration for both chlorine and stabilizer decrease and reach a steady state. The stabilizer decrease to zero (loss of stabilizer) because the stabilizer (antioxidant) were chemically consumed by chlorine, which is consistent with the literature [6]. The figure shows that chlorinated water rapidly degraded the antioxidants. The chlorine decrease

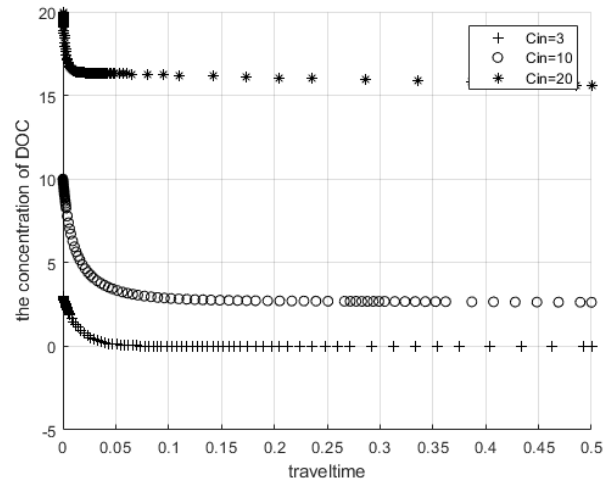
due to the action of the stabilizer but it remain in the system. Both of the numbers of chain scission and crosslinks increased concerning time before it reached the steady state. Polymer degradation started when the antioxidant system was depleted.



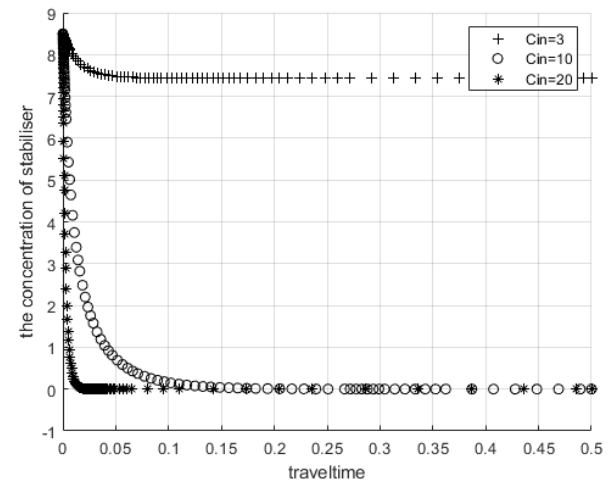
**Figure 2.** High DOC concentration (a) The profile of chlorine and stabiliser concentration (b) The number of chain scission and crosslink when  $H_{in}=8.5$  and  $C_{in}=10$ .

Figure 3 shows the profile of chlorine concentration for different initial values of DOC i.e.  $C_{in} = 3, 10, 20$ . As the initial DOC concentration is higher, the longer the DOC will remain in the system. For a low initial value of DOC, the chlorine depleted rapidly due to the action of stabilizer. On the other hand, Figure 4 indicates that the concentration of stabilizer varies for the various value of  $C_{in}$ . As  $C_{in}$  getting higher, the amount of stabilizer remained in the system is lower. The loss of stabilizer from the system is to increase as  $C_{in}$  increased. The time of depletion of antioxidant is shorter as  $C_{in}$  increase. The consumption of antioxidants in polyethylene containing different chlorine concentrations are the subject Figure 4.

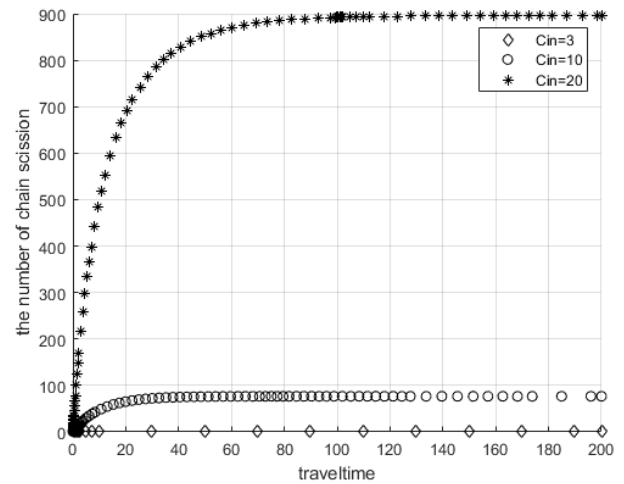
As  $C_{in}$  getting higher, the number of chain scission is higher, as illustrated in Figure 5. Similarly, the number of crosslink increase when the amount of chlorine added to the system increased (Figure 6).



**Figure 3.** The profile of chlorine concentration for different initial value of DOC.



**Figure 4.** The profile of stabiliser concentration for different initial value of DOC.



**Figure 5.** The number of chain scission for different initial value of DOC.

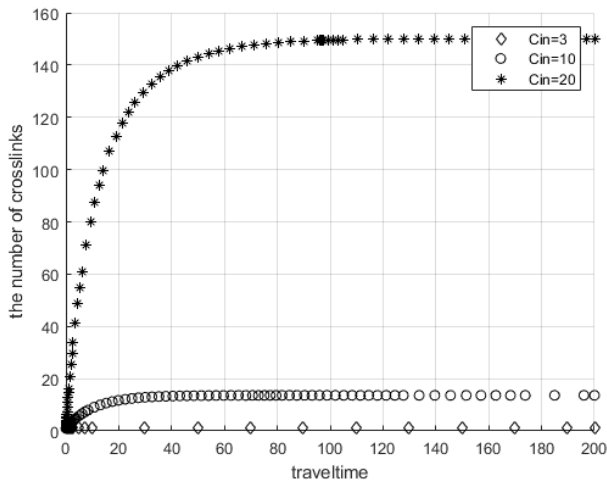


Figure 6. The number of crosslinks for different initial value of DOC.

## 4 Conclusion

In this paper, we employed the nondimensionalization technique for the kinetic model of corrosion process of polymer pipes that exposed to the chlorinated environment. We reduced the complex model to a set of simple equations. The behavior of the model between the high-concentrated initial value of chlorine dioxide and low-concentrated one is compared. We studied the effect of different DOC concentration on the model. The resulting approximate solutions capture some essential characteristics and provide insights into the system. This approach enables us to predict corrosion behavior without the necessity of extensive use of laboratory testing. It is found that mathematical analysis is in agreement with the laboratory

experiments recorded in the literature.

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