

## CFD Study of Chemical Vapor Deposition Reactor for Synthesis of PHEMA

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The current development of technologies related to materials for science, biology and medicine is gaining a new impetus in order to give a better treatment to injured tissues and organs. In this context, biomaterials and biofabrication techniques are providing a healthier life to the population. However, to produce implant parts and devices, there is the need for biocompatibility and absence of toxic materials, which may preclude their medical application. To avoid this situation, Chemical Vapor Deposition (CVD) is presented as an attractive technique, since it can produce, in some case solvent less, polymeric biomaterials and uniform adherent films over substrates in just one single processing step. The development of CVD reactors has been extensively studied, but little is known about their fluid dynamic behavior and associated heat and mass transfer effects. The aim of this paper was to simulate a CVD reactor during the synthesis of poly 2-hydroxyethyl methacrylate (PHEMA), through of the release of the gaseous 2-hydroxyethyl methacrylate (2-HEMA) and initiators in a single step, completely dry, without the use of solvents or volatiles. The impact of operating conditions in the quality and characteristics of the deposited material was explored. A computational fluid dynamic (CFD) study was carried out to simulate velocity and temperature distribution on the vertical CVD. As a result, certain design aspects related to heat and mass transfer were addressed, which allowed to understand and to suggest modifications in the reactor design. These simulations were important to define a desirable temperature operation range aiming a uniform flow distribution in the reactor.

### 1. Introduction

Biomaterials from poly 2-hydroxyethyl methacrylate (PHEMA) and its derivatives are fairly applied in tissue engineering because of their biocompatibility properties, its high water absorption capacity (>38%) without dissolution (polymeric hydrogels) (Nogueira et al., 2012) and similarities to living tissue. Porous materials based on this polymer are used as components of artificial corneas, scaffolds for neural regeneration and controlled drug release systems.

In situ polymerization, polymerization-induced phase separation (Paterson et al., 2012), ultraviolet or chemical vapor deposition (CVD) (Bose and Lau, 2011) are some ways to obtain PHEMA hydrogels. However, among such synthesis techniques, CVD becomes an interesting alternative for obtaining solvent-free biomaterials. Chemical vapor deposition involves the chemical reactions of gaseous reactants on the surface of a substrate. This bottom-up manufacturing process can provide highly pure coatings with precise control at atomic or nanometric scale (Aliofkhazraei and Ali, 2014).

Bose and Lau (2011) and previous work demonstrated the success of the CVD technique to produce films of PHEMA hydrogels. Results showed that the hydrogels obtained possessed appropriate properties for adhesion and proliferation of cells, viable for use as biomaterials. Despite the experimental results demonstrating the feasibility of the technique, generally, little is known about the heat and transfer phenomena taking place during the reaction and their impact on the final products properties that may drive biological

applications. In this sense, computational techniques able to represent suitably the fluid dynamics occurring in CVD systems are good tools to understand the process. The use of computational fluid dynamics (CFD) provides valuable information for the development, scale up and optimization of process equipment (reactors). In fact, in principle it is possible model the detailed interaction between physical/chemical processes and geometry (Hansen et al., 2013) and to obtain quantitative results on the behavior of the fluid and transport of species from reaction engines and transport properties (Li et al., 2006).

In this work a computational fluid dynamic model was developed, based on finite volume in the ANSYS platform, to simulate the temperature and velocity profiles of the reagents in the synthesis of PHEMA, in a vertical CVD reactor, under atmospheric pressure. Tert-butyl peroxide (TBPO) was used as a free-radical initiator. The peroxide bond is easily dissociated at low temperatures (<150 °C). Although vertical CVD reactors have been used for reactions involving carbon nanotubes, the literature is still lacking on the hydrodynamic aspects and the phenomena of heat and mass transfer in these systems (Mishra and Verma, 2012). The advantage of working with the reactor at atmospheric pressure involves the decrease of the equipment cost, reaction chambers of reduced size (Abedi et al., 2013) and good uniformity of the films deposited, as demonstrated in the work of Luo et al. (2004). The results, presented here, allowed to obtain more adequate information about the characteristics and behavior of the CVD reactor developed. Using such an approach it is possible to evaluate the flow of the reactive gases and the temperature distribution in the reactor.

## 2. Modeling and Numerical Simulation

The CFD simulations were performed in the software ANSYS CFX, which uses the finite volume method for solving the equations of momentum, mass and energy. The Eq (1), Eq (2) and Eq (3), in the steady state, describe such phenomena. Details of the numerical algorithm and procedures can be obtained in the user's Guide of the CFX.

Continuity equation

$$\nabla \cdot (\rho \cdot u) = 0 \quad (1)$$

Momentum conservation equation

$$\begin{aligned} \nabla \cdot (\rho \cdot u \otimes u) &= -\nabla p + \nabla \cdot \tau \\ \tau &= \mu (\nabla u + (\nabla u)^T) - \frac{2}{3} \delta \nabla \cdot u \end{aligned} \quad (2)$$

Thermal energy

$$\begin{aligned} \nabla \cdot (\rho \cdot u \cdot h) &= \nabla \cdot (\lambda \cdot \nabla T) + \tau : \nabla u + S_E \\ h &= \sum_i^{N_c} Y_i \cdot h_i \\ h_i &= h_{i, T_{ref}} + \int_{T_{ref}}^T c_{p,i} dT \\ S_E &= \sum_{j=1}^{N_r} (-\Delta H_R)_j \cdot R_j \end{aligned} \quad (3)$$

Where:  $\rho$  is the density;  $u$  is the speed;  $\tau$  is the tensor forces associated with the rate of shear;  $\mu$  is the dynamic viscosity;  $\delta$  is the identity matrix;  $Y_i$  is the mass fraction of component  $i$ ;  $R_j$  is the reaction rate of component  $j$ ;  $h$  is the thermodynamic enthalpy;  $\lambda$  is the thermal conductivity;  $T$  is the temperature;  $S_E$  is the term for power generation;  $c_{p,i}$  is the specific heat at constant pressure;  $\Delta H_R$  is the change in enthalpy of the reaction;  $P$  is pressure and  $R$  is the universal gas constant.

The solution of these equations provides results of interest (distribution of temperature and velocity profiles of the reagents) for the physical domain (geometry) of the problem. For this solution, the domain is discretized into control volumes, of micro- or nano-dimensions, in which a physical quantity or property maintains an average value under the same conditions reproducible in laboratory, while retaining the same working conditions (Maliska, 2003).

In this study, the three-dimensional geometry of the CVD reactor was developed in CAD software (computer-aided design). A total of 1.753.943 numeric cells were used for the simulation, taking into consideration the different regions of the reactor: reaction zone, area of deposition, fluid entry and exit. In order to provide stable and accurate numerical solutions the range of mesh quality values (aspect ratio, expansion factor and orthogonal angle) were considered good according to Ansys 14.5 Manual (2012).

### 2.1 Boundary Conditions

For the boundary conditions, the CAD file was imported into the CFD software, and the values shown in Table 1 were defined. In this work, the natural convection was considered and estimated from the models of

Incropera et al., (2011), exerting influence in the heat exchange with the extern wall of the reactor. Considering the operational conditions of the problem, the Reynolds numbers were low, from 4.06 (T1.2.1) to 87.70 (T1 and T7), which suggests a purely laminar flow regime. Low Reynolds numbers combined with wide temperature differences can lead to significant interactions between forced convection and natural convection on the CVD equipment, strongly influencing the flow of gas, chemistry and heat and mass transfer in high pressure systems (Kleijn et al., 2007).

Table 1: Boundary conditions

Heat Transfer Coefficient (W / m <sup>2</sup> K)	11
Reaction Zone Temperature (° C)	225
Temperature of the Area of Deposition (° C)	25
Flow of HEMA (mL / h)	5-10
Flow of TBPO (mL / h)	1-2
N <sub>2</sub> flow (mL / min)	10-100
Wall Temperature in the Reaction Zone (° C)	25-200
Flow of Coolant (Kg / s)	0.00177

A convergence criterion of  $1 \times 10^{-5}$  was applied to the residues (RMS – Root Mean Square) of the equations of mass balance, continuity, momentum and energy. All simulations were performed under laminar and steady state conditions. Table 2 depicts the planning used in the simulations. It was evaluated the temperature, initial flows of the reagents, temperature of the reactor wall (reaction zone), temperature of the area of deposition and flow of the carrier gas (nitrogen- N<sub>2</sub>).

Table 2: Planning of the simulations (Flow of HEMA and TBPO at mL / h; N<sub>2</sub> flow at mL / min)

Identification	HEMA: N <sub>2</sub>		TBPO: N <sub>2</sub>		Entry temperature of the reagents (° C)		Reactor temperature (° C)	
	HEMA	N <sub>2</sub>	TBPO	N <sub>2</sub>	HEMA	TBPO	Reaction Zone	Deposition Area
T1	10	100	2	20	225	110	25	25
T2	7.5	75	1.5	15	225	110	25	25
T3	5	50	1	10	225	110	25	25
T4	7.5	75	4	40	225	110	25	25
T5	7.5	75	2	20	225	110	25	25
T6	7.5	75	1	10	225	110	25	25
T7	10	50	2	10	225	110	25	25
T8	10	100	2	20	175	60	25	25
T1.1	10	100	2	20	225	110	100	25
T1.2	10	100	2	20	225	110	150	25
T1.3	10	100	2	20	225	110	200	25
T1.2.1	10	100	2	20	225	110	150	5

Table 3: Heat capacity, specific heat, viscosity and thermal conductivity of the CVD precursors

Properties	HEMA	TBPO
Viscosity (N.s / m <sup>2</sup> )	$\ln \eta^{*J} = -14.89952 + \frac{2907.746}{T}$ $288.15 \leq T \leq 318.15$	$\ln \eta^{*J} = -15.39346 + \frac{4616824}{T} - \frac{9129558}{T^2} + \frac{90524680}{T^3}$ $270 \leq T \leq 550$
Specific heat/ Heat Capacity	$1.97(J / g^{\circ}C)$	$y = 598.57T + 117472$ (J / Kmol.K)
Thermal Conductivity (W / m.K)	$y = 9 * 10^6 T^{-2.509}$	$\lambda^{*J} = 0.1472703 - 2.05 * 10^{-5} T - 2.64 * 10^{-7} T^2$

Table 3 presents the values of heat capacity, viscosity, specific heat and thermal conductivity of the CVD precursors (HEMA and TBPO) from data estimated in the software Aspen Plus and in the calorimeter DSC Mettler Toledo 823e.

### 3. Results and Discussion

#### 3.1 Temperature Distribution

The results obtained from the simulations allowed to evaluate the impact of the temperature profile on the fluid velocity. Figure 1 presents the distribution of the temperature of experiments T1 to T7, where the temperature of the reaction zone and area of deposition were held constant.

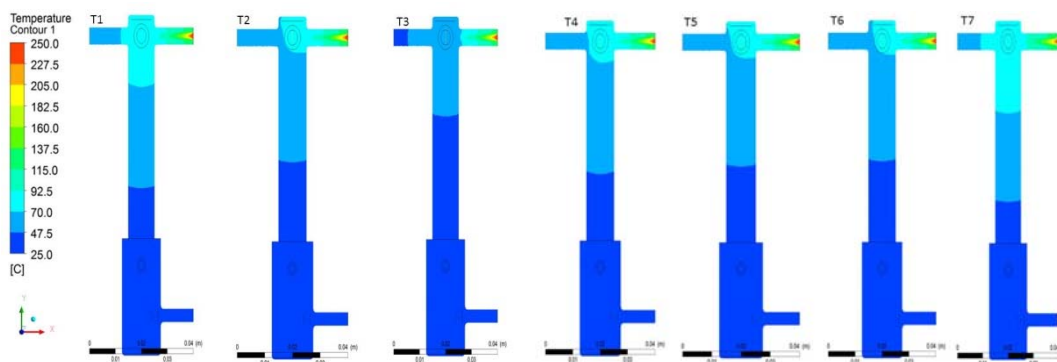


Figure 1: Distribution of the temperature of experiments T1 to T7

It is possible to observe through experiments T1, T2 and T3, that the smaller the initial flow of reagents, the lower the temperature obtained in the reaction zone, considering only the loss of heat by natural convection in the CVD reactor wall.

The influence of the TBPO initial flow on the distribution of the temperature inside the CVD reactor can be noted in T4, T5 and T6. This variable did not have synergistic effect on the temperature. By quadrupling the initial TBPO flow (T4), the distribution is practically the same when compared to experiments T5 and T6. The reaction zone presented a temperature between 47.5 and 92.5 °C and the area of deposition, a temperature between 47.5 and 25 °C.

When comparing T1 and T5, and T3 and T6, in Figure 1, it can be seen the influence of the entry flow of the HEMA monomer on the distribution of the temperature. A flow rate of 10 mL / h, at 225 °C, although it does not change the temperature in the area of deposition, provides a temperature range from 70 to 92.5 °C in greater lengths along the reactor.

The nitrogen flow effect or reactant / N<sub>2</sub> ratio was verified in experiments T1 and T7. The flow of gas has an important role over the control of the rate and uniformity of the deposition, since it is this variable that governs the supply of reagents to the substrate, which may be limited by the mass transport (Barbosa et al., 2006).

Results showed the lower the N<sub>2</sub> flow, the greater the temperature of the fluids obtained in the center of the reactor. The carrier gas flow (N<sub>2</sub>) has a cooling effect and must be included to give a correct temperature distribution. According Mitrovic et al., (2007) increases the total flow rate of the carrier gas may allow higher operations pressures and high deposition rates. At the same time, this effect can reduce the deposition rate due to the greater dilution of reagents fluids.

Figure 2a reveals the effect of (external) natural convection on the temperature distribution inside the CVD reactor. In T1, the reactor wall, in the reaction zone, is kept at room temperature and is influenced by the convective heat transfer coefficient (11 W / m<sup>2</sup> K). The convective term, in turn, increased the computational time from 23 min to 83 min. The convective heat loss is relatively high for a mean entry temperature of the reagents at 167.5 °C. The value of the temperature at the center reaches approximately 55 °C. However, when maintaining a temperature of 100 °C (T1.1) in the reactor wall, there is a temperature distribution from 92.5 °C to 115 °C in reaction zone, but it is possible to maintain the same temperature range in the area of deposition than T1 experiment (25 to 47.5 °C). The cooling fluid (water) allows a temperature constancy of the unreacted exit fluid.

For CVD reactions of vinyl monomers, the hot filament temperature (reaction zone) is normally between 200-300 °C (Chan e Gleason, 2005a). Under the conditions studied, the calorimeter DSC presented a temperature of polymerization of HEMA and TBPO at 150 °C ± 5 °C (graph not shown).

Figure 2b shows the study the heating in the reaction zone at different temperatures, so that the fluid can stay at a temperature appropriate for polymerization. The reactor is assumed to remain at the constant temperatures of 100 °C (T1.1), 150 °C (T1.2) and 200 °C (T1.3). The results allowed to conclude that a

minimum heating of 150 °C is appropriate to ensure better temperature uniformity in the desired reaction value, with distribution profiles from 137 to 160 °C (T1.2).

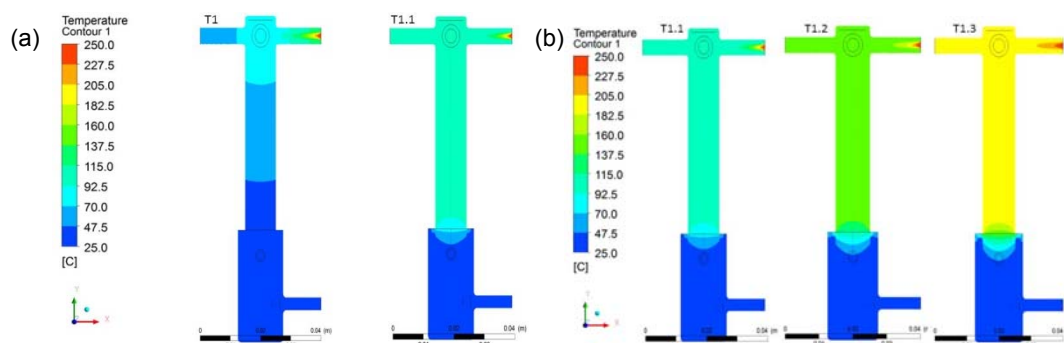


Figure 2: a-Effect of the natural convection on temperature distribution of the CVD reactor; b-Temperature distribution profile for different heating in the reaction zone

The influence of the temperature distribution in the zone of deposition (substrate;  $-0,03 \leq Y \leq 0$  m) was verified in Figure 3a. Experiments T1.2 and T1.2.1 demonstrate that the temperature of the cooling fluid (water) at 25 °C and constant flow of 0.00177 Kg / s is sufficient to cool the area of deposition and the substrate at temperatures in the range from 25 to 47.5 °C, which avoids energy expenditure. The temperature distribution profiles are virtually superimposed, without interference in the reaction zone. According to Chan e Gleason 2005b, the values for the substrate temperature are suitable between 20-50 °C. Parameters such as flows of reagents (T1, T2 and T3) and flow of carrier gas (T7) also did not interfere with the substrate temperature.

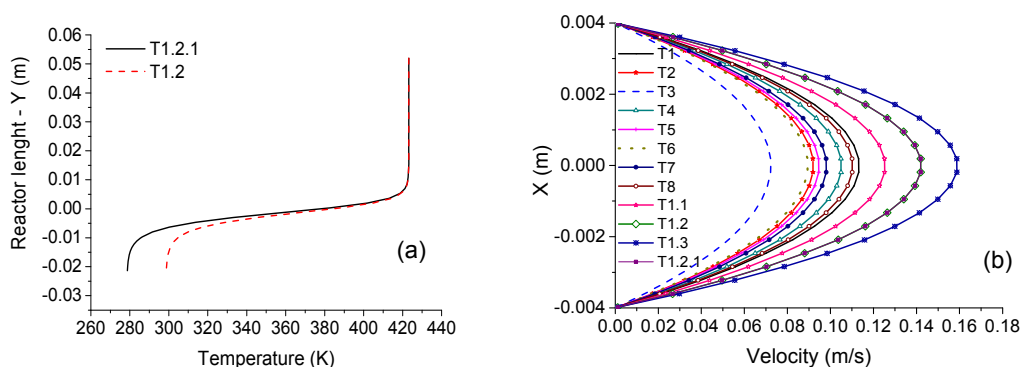


Figure 3: a-Temperature distribution throughout the length of the reactor  $-Y$  (T1.2 and T1.2.1) at 50 different points (vertical); b- Velocity profiles in the X direction of the CVD reactor.

### 3.2 Velocity

The effect of the velocity of the reagents has significant importance in the interaction with the substrate. Figure 3b shows the velocity profile of the reactive fluids inside the CVD reactor. The maximum velocity of 0.113 m / s was achieved in experiment T1 and the minimal velocity of 0.072 m / s, in experiment T3. When comparing T1 to T5 (0.094 m / s) and T7 (0.098 m / s), it is possible to verify that the predominant effect is the total mass flow of the reagents. The higher the mass flow of the system, the greater the velocity in the center of the reactor, although a 50 % reduction in carrier gas fluid (T7) does not interfere so strongly in the final velocity. The same effect is observed when comparing experiments T4, T5 and T6. A four times increase in the TBPO initial flow increases the velocity at the center of the reactor from 0.089 (T6) to 0.105m / s (T4).

The effect of the entry temperature of the reagents on velocity can be seen in experiments T1 and T8. A temperature difference of 50 ° C showed little significance on velocity. Rounding the values of the velocities obtained in two decimal places, the resulting velocities are the same: 0.11 m / s. The difference between the values is 0.004 m / s.

The effect of temperature on the velocity of the reagents is also demonstrated in Figure 3b (T1, T1.1, T1.2, T1.3 and T1.2). It can be noted that the higher the temperature in the reaction zone, the greater the velocity obtained in the center of the reactor. By nature, the axial velocity is parabolic and gradually increases to a

maximum value where the temperature of the fluid is higher. The velocity values obtained are, respectively, 0.113 m / s at 25 °C (T1), 0.125 m / s at 100 °C (T1.1), 0.142 m / s at 150 °C (T1.2) and 0.159 m / s at 200 °C (T1.3). The experiments T1.2 and T1.2.1 did not suffer variation in the velocity profiles. This allowed to conclude that the temperature in the zone of deposition does not interfere in the variable analyzed, within the range of study. The result of the simulations led to a better velocity in 0.142 m / s, considering the influence of temperature and flows of fluids.

#### 4. Conclusions

In the present work, the CFD computational tool was used to investigate the velocity and temperature profiles during PHEMA synthesis in CVD reactors. The parameters that affect the uniformity of the product were evaluated from the geometry of the reactor at atmospheric pressure. In addition, the results showed that it is possible to have information and understand the system behavior in such way to build CVD reactors from fluid dynamics simulations, which leads to a great development of equipment without the need for large investments and/or high process costs related to try and errors procedures. Therefore, CVD reactors may have design details specified, before their physical manufacturing, and the process conditions can be quickly estimated.

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