

Numerical simulation of polymers-carbon nanotubes mixing process

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Abstract

This paper focuses on the numerical simulation of polymer mixing process. The polypropylene has been mixed with different MWCNTs contents. A two dimensional numerical simulation of the polypropylene/ multi-walled carbon nanotubes (PP/MWCNT) has been investigated showing the flow into a twin-screw mixer. The velocity, the shear-rate and the temperature has been carried out with taking into account the thermal coupling.

Keywords: Mixing process, thermal coupling, velocity filed, shear-rate filed, polypropylene/multi-walled carbon nanotubes.

Résumé

Cette communication concerne le procédé de mélangeage de polymères avec des nanotubes de carbone. Nous proposons une simulation numérique bidimensionnelle de l'écoulement des polymères chargés en nanotubes de carbone dans le mélangeur indiquant le champ de vitesse, le champ de température et le taux de cisaillement dans la chambre de mélangeage, en prenant en compte le couplage thermique. Ensuite on aborde la, et nous avons calculé le champ de vitesse et de température durant la phase de mélangeage.

Mots clés: Procédé de mélangeage, champ de vitesse, taux de cisaillement, champ de température, couplage thermique, polypropylène chargé par des nanotubes de carbonnes

1. Introduction

Since their official discovery in 1991 by Iijima [1], carbon nanotubes characteristics are growing in the field of science and engineering: their mechanical and physical properties make CNT as attractive candidates for composite materials (polymer/CNT) and applications. These mechanical performances strongly depend on the composite melting. Many studies have been carried out by several authors and referenced by Coleman et al. [2] and Breuer and Sundaraj [3].

One of the most important parameters during the elaboration of polymers/CNT composites is the nanotubes dispersion in the polymer matrix. Indeed it is critical for reinforcing the efficiency because the strong tendency of nanotubes to nanotubes aggregation when they are mixed significantly affects the mechanical properties of the resulting composite material. Many investigations on carbon nanotubes dispersion in the polymer matrix have been carried out and a part of them are related in this paper.

Comsol® software has been chosen for modeling the CNT-polymer mixing process because of its capabilities for solving multiphysic coupled problems. A proper description of the

PP/MWCNT physics flow is obtained. This FEM analysis appears as a first step for the simulation of three dimensional mixing of PP/MWCNT composites. In our research, the mixing experiments were carried out using a Brabender® mixer (Plastograph EC W50EHT, Fig. 1), that allows to process with batch mixtures up to 40 cm³. The temperature in the mixing cavities is regulated. The blades are made of special steel. Counter-rotation towards each other at different speeds provides excellent compounding and mixing characteristics, the speed ratio driven at idle blade is about 2:3. As it is shown in Fig. 3, the fluid is contained in the cavity enclosed by the frame and the two screws. The left screw rotates in the clockwise while the right one rotates in the counter clockwise. Both mixing torque and the temperature are measured using sensors and software

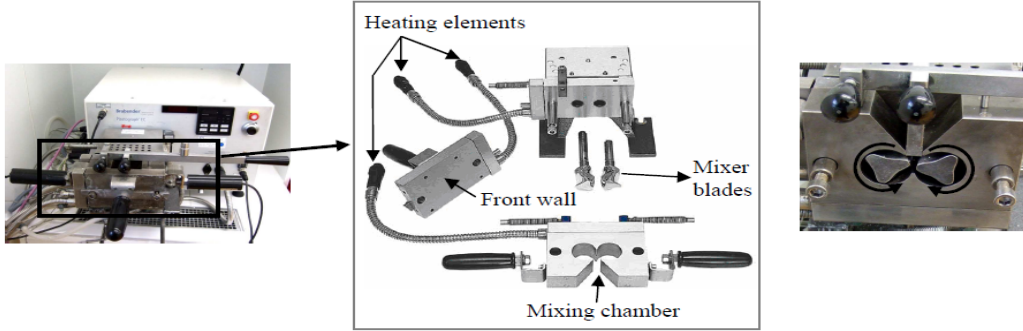


FIG. 1 - Twin screw mixer (velocity max. 150 rpm, max. temp 500°C)

2 Modeling and numerical simulation

2.1 Governing equations

An Arbitrary Lagrangian–Eulerian (ALE) approach with moving mesh on both Ω_2 and Ω_3 sub-domains is used to discretize the problem as shown by Thiébaud F, Gelin J [4]. By considering the above geometrical data, the solution of the coupled fluid flow–thermal problem allows us to calculate:

The velocity field: $\vec{V}(x, y, t) = V_x(x, y, t)\vec{x}_1 + V_y(x, y, t)\vec{y}_1$

- The pressure field : $p(x, y, t)$.
- The temperature field : $T(x, y, t)$.

The velocity field and the pressure are governed by the following Navier–Stokes equations:

The temperature variation is governed by the heat equation, given by the Eq. (3):

$$\text{div}\vec{V} = 0 \text{ into } \Omega_1 \cup \Omega_2 \cup \Omega_3 \quad (1)$$

$$\rho \frac{d\vec{V}}{dt} = -\overrightarrow{\text{grad}}(p) + \mu(\dot{\gamma}, T)\vec{\Delta}(\vec{V}) \quad (2)$$

$$\rho C_p \left\{ \frac{\partial T}{\partial t} + \overrightarrow{\text{grad}}(T) \cdot \vec{V} \right\} + \text{div}(\vec{q}) = 2\mu(\dot{\gamma}, T)\vec{\dot{\epsilon}} : \vec{\dot{\epsilon}} \text{ into } \Omega_1 \cup \Omega_2 \cup \Omega_3 \quad (3)$$

where C_p is the specific heat coefficient, $\mu(\dot{\gamma}, T)$ is the shear viscosity, $\dot{\gamma}$ is the equivalent shear rate and $\vec{\dot{\epsilon}}$ is the shear rate tensor. The Fourier's law is:

$$\vec{q} = -K \cdot \overrightarrow{\text{grad}}(T) \quad (4)$$

where $\vec{q}$ is the heat flow, K is the thermal conduction coefficient. The heat equation becomes:

$$\rho C_p \left\{ \frac{\partial T}{\partial t} + \overrightarrow{\text{grad}}(T) \cdot \vec{V} \right\} - K\Delta T = 2\mu(\dot{\gamma}, T)\vec{\dot{\epsilon}} : \vec{\dot{\epsilon}} \text{ into } \Omega_1 \cup \Omega_2 \cup \Omega_3 \quad (5)$$

$$\rho = \left(\frac{f}{\rho_c} + \frac{1-f}{\rho_p} \right)^{-1} \quad (6)$$

where f is the mass fraction of the MWCNT, ρ_c is the Multi-walled Carbon Nanotube (MWCNT) density and ρ_p is the density of polypropylene.

The boundary conditions to be considered for this problem are the following:

Frame and screws walls adhesion: $\vec{V}_{/Ri} = \vec{0}$ on $\partial_1\Omega \cup \partial_2\Omega \cup \partial_3\Omega$ into the local frame. Open boundary condition at the mixer inlet: $\vec{\sigma} = 0$ on $\partial_4\Omega$. Imposed temperature on the screws and the frame: $T = 473K$ on $\partial_1\Omega \cup \partial_2\Omega \cup \partial_3\Omega$. External heat transfer at the inlet of the mixer is: $-K \cdot \overrightarrow{\text{grad}}(T) = h(T - T_{ext})\vec{n}$ on the $\partial_4\Omega$, where $\vec{\sigma}$ is the stress tensor defined vs viscosity and pressure.

$$\vec{\sigma} = -p\vec{I} + 2\mu(\dot{\gamma}, T)\vec{\epsilon} \quad (7)$$

where T_{ext} is the external temperature fixed at 293 K, Furthermore, continuity equations must be considered at the moved/fixed frames boundaries $\partial_{12}\Omega$ and $\partial_{13}\Omega$. These equations can be written as following for the mechanical problem

$$\vec{\sigma}_1 - \vec{\sigma}_2 = 0 \text{ on } \partial_{12}\Omega \quad (8)$$

$$\vec{\sigma}_1 - \vec{\sigma}_3 = 0 \text{ on } \partial_{13}\Omega \quad (9)$$

where $\vec{\sigma}_{i=1,2,3}$ is the stress tensor of $\Omega_{i=1,2,3}$

and in the following form for the thermal problem

$$(\vec{q}_1 - \vec{q}_2)\vec{n}_{12} = 0 \text{ on } \partial_{12}\Omega \quad (10)$$

$$(\vec{q}_1 - \vec{q}_3)\vec{n}_{13} = 0 \text{ on } \partial_{13}\Omega \quad (11)$$

where $\vec{q}_{i=1,2,3}$ is the heat flow of $\Omega_{i=1,2,3}$

The initial conditions are:

$$V(t=0) = V_0 = \vec{0} \quad (12)$$

$$p(t=0) = p_0 = 0 \quad (13)$$

$$T(t=0) = T_0 \quad (14)$$

where V_0 , T_0 and p_0 are respectively the initial velocity, the initial temperature T_0 fixed to 423K, and the initial pressure.

The equations of the moving frame are:

$$\begin{aligned} \overrightarrow{OM_1} &= [(x - x_0) \times \cos(-\omega_i t) - (y - y_0) \times \sin(-\omega_i t) - (x - x_0)]\vec{x} \\ &\quad + [(x - x_0) \times \sin(-\omega_i t) + (y - y_0) \times \cos(-\omega_i t) - (y - y_0)]\vec{y} \\ \overrightarrow{OM_2} &= [(x - x_0) \times \cos(\omega_i t) - (y - y_0) \times \sin(\omega_i t) - (x - x_0)]\vec{x} \\ &\quad + [(x - x_0) \times \sin(\omega_i t) + (y - y_0) \times \cos(\omega_i t) - (y - y_0)]\vec{y} \end{aligned} \quad (15)$$

where (x_0, y_0) are the distances between o and the extremity $M_{i=1,2}$ of the domain $\Omega_{i=1,2}$, (x, y) are the Cartesian coordinates, t is the time, and ω_i angular speed of each blade.

2.2 FEM simulations

COMSOL Multiphysics (formerly FEMLAB) is a finite element analysis, solver and Simulation software / FEA Software package for various physics and engineering

applications, especially coupled phenomena, or multiphysics. COMSOL Multiphysics also allows for entering coupled systems of partial differential equations. Comsol Multiphysics software has been used to implement the proposed model and to perform the 3D simulation.

2.3 Two dimensional mixing simulation

The geometry that is treated is associated to the mixer described in figure 1. The model is based on the Navier-Stokes equations formulated with a rotating frame in the inner sub-domain and in fixed coordinates in the outer one. At the fixed boundaries no-slip boundary condition is applied. At the inlet and outlet, the normal stress is set to zero. The implementation, using the Rotating Navier-Stokes predefined multiphysics coupling, is quite straightforward. The characteristics of the polymer are shown in the table below. The computational time corresponds to 1.58min. The computer's characteristics are: CPU : Intel® Pentium® Dual 2.00GHz and RAM: 2.00Go.

In that section one relates the neat PP and PP/MWCNT composites flow into the Brabender® mixer during the mixing stage. A two dimensional (2D) problem is considered as an approximation of the section screw, one considers a laminar and incompressible flow without external (polymer + fiber) loading as shown by Haas A, Scholle M, Aksel N, Thompson H M, Hewson R W, Gaskell P H [5]. The material domain Ω is divided into three sub-domains described in figure 3.

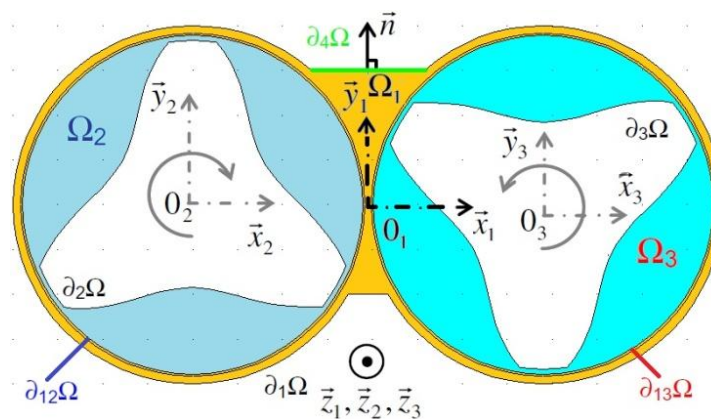


FIG. 3 - Moving and fixed frame, sub-domains and boundaries definition.

Physical characteristics	Value	Nomenclatures
$c_p (J.kg^{-1})$	2096	Specific heat coefficient
$K (W m^{-1}kg^{-1})$	0.233	Thermal conduction coefficient
$\rho_c (kg/m^3)$	1300	Density of MWCNT
$\rho_f (kg/m^3)$	900	Density of polypropylene
$f (%)$	8	Mass fraction of MWCNT

TAB. 2 - Thermal parameters for the neat PP for PP/MWCNT composite.

The fluid-thermal model has been implemented and can be assimilated to a multiphysic coupled problem between the “fluid flow module” (for the fluid problem), “heat transfer module” (for the thermal problem) and the “ALE moving mesh module” (for the moving meshes). The number of quadratic elements in Ω_1 is 241, in Ω_2 is 2046 and in Ω_3 is 2090, the total number of elements is 4377 with 2523 nodes (Fig. 4). An explicit time stepping scheme is used for the time dependant solver algorithm. The solution is given on the actual frames at each time step until $t_f = 3.5s$.

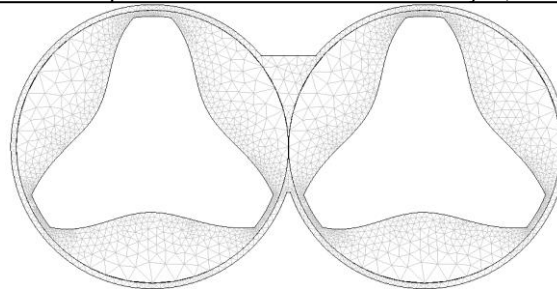


FIG. 4 - Mesh definition related to the twin screws mixer FE model (30795 DOF).

2.4 Results and discussions

The following results are related to the PP/MWCNT composite with 8 wt.% MWCNT content. One can notice that the maximum value for the velocity field is located at the middle of the frame and at the blades extremity. In addition, wall adherence conditions on the frame $\vec{V} = \vec{0}$ are respected.

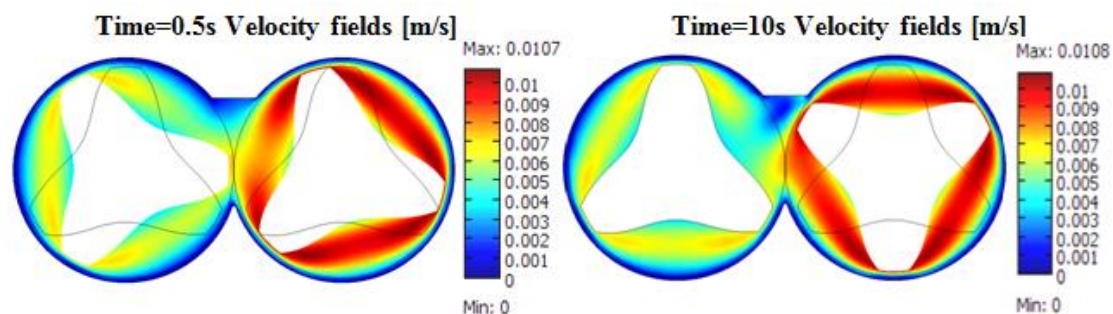
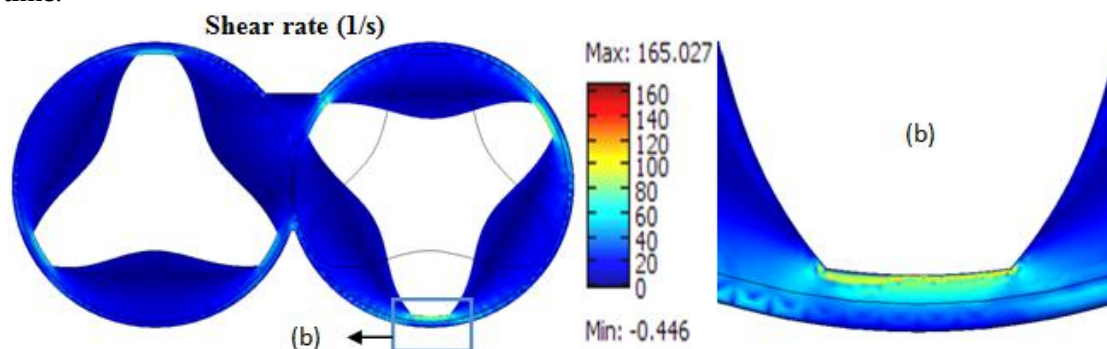


FIG. 5 - Velocity fields (in mm/s) at several time steps for the 8 wt.% PP/MWCNT

The shear rate is represented in Fig. 6, at $t = 5$ s. These figures reveal that the shear rate is approximately constant in the cavity except near the screws extremity where the shear rate is very higher than in the cavity. One can affirm that the mixing phase is effective near the screw extremity (at high shear rate). Furthermore, the shear rate field is practically constant in time.

FIG. 6 – Shear-rate (in 1/s) at $t= 5$ s for the PP/MWCNT

The temperature fields are related in Fig.7. At the beginning of the simulation, the PP/MWCNT composite temperature is globally equal to 423°K except on the frame and screws walls, where the temperature is imposed ($T = 473^\circ\text{K}$). During the simulation, the temperature in the cavity increases up to limit value equal to 473°K, corresponding to the imposed mixing temperature on the frame and screws walls. This simulation clearly reveals that the mixing temperature is quickly reached, which guarantees optimal mixing conditions. The heat transfer influence at the mixer inlet is related in figure that relates that a significant

variation of the temperature in the middle of the cavity, where the temperature is practically equal to the PP melting temperature.

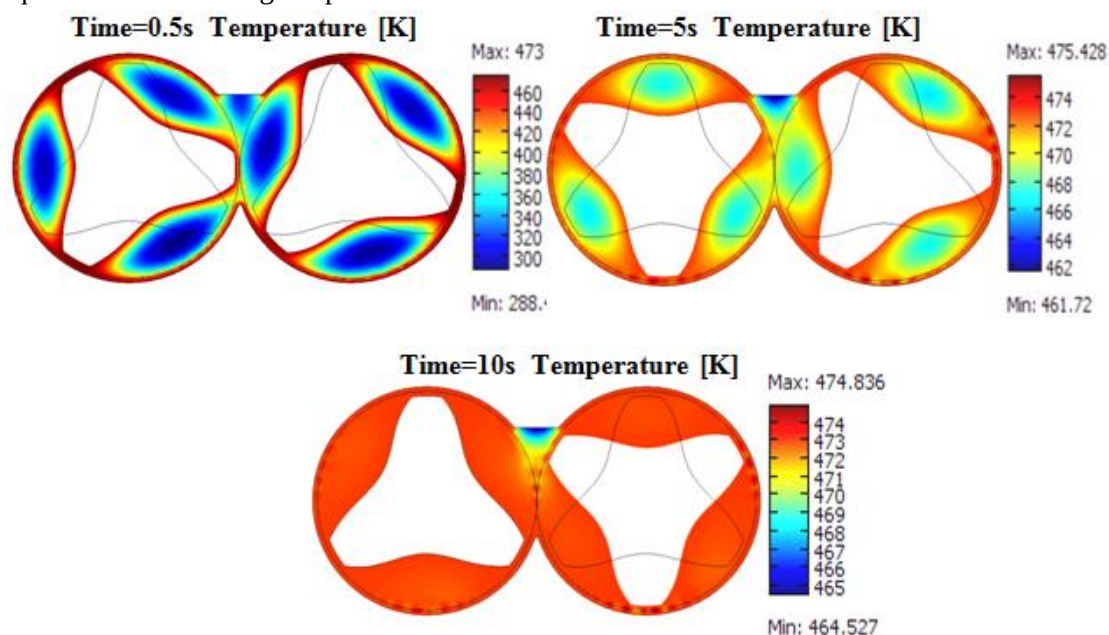


FIG. 7 - Temperature field (in K) at several time steps for the 8 wt.% PP/MWCNT

3. Conclusions and prospects

The physical modeling and numerical simulations of PP/MWCNT composite flow in a twin-screw mixer at high shear rates has been investigated in this paper, based on an appropriate finite element modeling of the composite flow during the mixing process. The reported finite element simulations allow to account the velocity effects, as well as temperature contours and provide a well founded basis for the simulations of the PP/MWCNT composite in the mixer according a multiphase model developed at the microscale.

The complete 3D modeling and simulation problem now is ongoing and it will permit to establish an accurate modeling tool for the development of a computational methodology of carbon nanotubes loaded polymers, as well as for establishing the resulting physical and mechanical properties with mixing and injection modeling.

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