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Characterization of rheological behaviors of polypropylene / carbone nanotubes composites and modeling their flow in a twin screw mixer

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Abstract

This paper focuses on the numerical simulation of the polypropylene / multi-walled carbon nanotubes (PP/MWCNT) flow into a twin screw mixer, during the mixing phase. The PP/MWCNT behavior obeys an innovating Carreau law enriched temperature built on the rheological properties carried out previously. The polypropylene was mixed with different MWCNTs contents (1, 2, 4 and 8 wt% of MWCNT content) and the rheological tests were performed at shear rate ranges from 10^{-1} to $2 \cdot 10^4 \text{ s}^{-1}$ at four temperatures (180, 200, 220 and 240 °C). Thus the effects of the temperature and the MWCNTs content on the rheological properties of the PP/MWCNT composites were investigated. The finite element (FEM) analysis of the PP/MWCNT flow allows to compute the velocity, the shear rate and the temperature during the mixing phase period. A good agreement between the experimental measured torque on the screw and the calculated one is shown. Therefore, one can consider that the physical flow is generally well described, awaiting a numerical simulation of the PP/MWCNT mixing phase.

1. Introduction

Since carbon nanotubes (CNT) official discovery in 1991 by Iijima [1], their interests have grown 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 melt process. Many studies have been carried out by several authors and referenced by Coleman et al. [2] and Breuer et al. [3]. One of the most important parameters during the elaboration polymers/CNT composites is the nanotubes dispersion in the polymer matrix. Indeed It is critical for reinforcing the efficiency because the relative ease of nanotubes to nanotubes sliding when they are assembled in ropes significantly affects the mechanical properties of the resulting material. Many investigations on the nanotubes dispersion in the polymer matrix have been carried out and a part of them are cited in this paper. Shear mixing by melt processing is one of the most current methods [4]. Nevertheless, most of studies are experimental ones.

In the present paper, one proposes an investigation about a polypropylene / multi-walled carbon nanotubes (PP/MWCNT) composite flow into a twin screw mixer through a finite element based simulation.

In the first part, PP/MWCNT composites were built with 1, 2, 4 and 8 wt% of MWCNT. During the preparation of PP/MWCNT composites, one has to ensure a proper dispersion of the nanotubes in the PP matrix. Generally, two methods are investigated: the first one consists in mixing the nanotubes and the polymer in a suitable solvent before evaporating it to form a composite film. It facilitates nanotubes debinding through the polymer and their dispersion. Jin et al [6], Shaffer et al. [7], or Qian et al. [8] were the first to investigate such a process by using the related method.

Nevertheless, this method is unsuitable for many polymers that can not be debinded. Melt processing is a common alternative that is particularly useful in the case of thermoplastic polymers and particularly polypropylene type. In general, melt processing involves the

melting of polymer pellets to form a viscous liquid. Carbon nanotubes are mixed into the melt by shear mixing. Then, bulk samples can then be realized using different process such as compression molding, injection molding or extrusion. An early study on the melt mixing of polymer and nanotubes was carried out by Jin et al. [9]. Andrews et al [10] showed that commercial polymers like polypropylene could be melt with carbon nanotubes to form composites. In addition, very good nanotubes dispersion was observed by Pötschke et al. [11] after blended batches of MWCNT in polycarbonate (PC) using a microcompounder at 260 °C. The authors clearly show that melt mixing is a powerful method to disperse nanotubes into polymers, and to load polymers, particularly polypropylene.

Thus, the rheological behavior of the neat PP and the PP/MWCNT composites are investigated by using a capillary rheometer. This investigation allows us to identify the rheological behavior for each PP/MWCNT composite and the neat PP by using a modified Carreau law enriched temperature. A few studies are reported on the rheological properties of polymer/nanotubes composites prepared by melt mixing process. Teng et al [12] investigated the effect of MWCNTs content on the rheological properties of polypropylene at high shear rates (10^2 to 10^4 s⁻¹) and a temperature around 200 °C. Thus, the authors proposed a power law as a constitutive model to characterize the rheological behavior of the composite. A similar study led by Seo et al. [13] focus on the rheological behavior of PP/MWCNT composite at low shear rates (10^{-1} to 10^2 /s) at a temperature about 170 °C. These investigations clearly show a dependence of the shear viscosity versus the shear rate at fixed temperature (200 °C and 170 °C respectively).

In the second part, this Carreau temperature law enriched is used to analyze the flow behavior of the composite into a twin screw mixer. The Comsol® software has been chosen because of its ease to for solving multiphysic coupled problems. The velocity, the shear rate and the temperature fields were also investigated. Finally, a comparison between the experimental and the calculated resulting torques on one screw has been carried out. A good agreement between the experimental measured torque on the screw and the calculated one shows that a good

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description of the PP/MWCNT physics flow is obtained with the uses of this original Carreau law enriched temperature. This FEM analysis appears as a first step for a next simulation of the mixing phase of PP/MWCNT composites.

2. Preparation of the PP/MWCNT composites

2.1. Materials characterization

Multiwalled Carbon Nanotubes (MWCNTs) were produced by Chemical Vapor Deposition (CVD) process and were supplied by NANOCYL[®] S.A., (Sambreville, Belgium). The purity of MWCNTs is more than 95%. In order to disperse MWCNTs, an experimental protocol developed by Ruan et al. [5] was used. MWCNTs powder was dispersed by using Sodium Dodecyl Sulfate (SDS) stands for surfactant and ultrasonic process. Thus, it was possible to observe MWCNTs through SEM images ($\times 60\,000 - 5\text{ kV}$) as shown in Figure 1. Nevertheless, it remains difficult to evaluate the dimensions of these MWCNTs. On considers that the diameter of MWCNTs is around 10 – 20 nm and the length is around 1 – 25 μm , their density is evaluated as $\rho_c = 1.30\text{ g/cm}^3$, according to the specifications of the provider.

Polypropylene is one of the most commonly used thermoplastic polymers which has been used in automobiles, appliances, construction, housewares, etc. Polypropylene is usually mixed with reinforcement or filler to improve its properties. The polypropylene in pellets form was a PP1120 type that corresponds to a homopolymer with a Melt Flow Indice (MFI) around 15 g/10min (230 °C, 2.16 kg). This PP grade is dedicated to injection molding and its density is evaluated as $\rho_p = 0.90\text{ g/cm}^3$.

2.2. Manufacturing phase

In our work, the mixing experiments were realized with a Brabender[®] mixer (Plastograph EC W50EHT, Figures 2 and 3), that allows to realize batch mixtures up to 40 cm^3 . The temperature in the mixing cavities and the rotation speed of the screws are regulated. As it is shown in Figure 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. The torques and the temperature have been measured using sensors and the associated software provided with the equipment. Polypropylene was mixed with various MWCNT mass fraction f : ($f = 1, 2, 4$ and 8 wt%) by drawing one's inspiration from the protocol described by Pötschke et al. [11]. Typically, the temperature in the mixing cavities and the rotation speed of the screw are regulated around $200\text{ }^{\circ}\text{C}$ and 60 rpm respectively, the process time is 15 min. Thus, bulk samples are collected and crushed into small particles in a grinder.

The measured mixing torque versus time is shown in Figure 4. One notices that the mixing torque increases with MWCNT content except for the batch corresponding to 1 wt%. As a general tendency, the mixing torque decreases with time to a limit torque. It can be related to the temperature of the PP/MWCNT composite increases until the imposed temperature, resulting in a decrease of the polypropylene shear viscosity. Due to the solid state of the PP/MWCNT composite when it is introduced into the mixer, very high values of the mixing torque are measured (increase of 300% compared to the torque measured after 10 min for each MWCNT content) until 3 min. Thus, because of heating into the cavity, the PP is softened, resulting in a rapid decrease of the mixing torque. It takes around 5 min to introduce PP/MWCNT composite at solid state into the mixer. It explains the fact that the beginning of effective mixing phase starts after 6 min.

3. Rheological properties of MWCNT/PP composites: results and discussion

3.1. Rheological measurements

In order to build a consistent law for the rheological behavior of the PP/MWCNT composites versus shear rate and temperature, the shear viscosity is measured on a very large shear rate range : (10^{-1} to $2 \cdot 10^4\text{ s}^{-1}$) at four temperatures ($180, 200, 220$ and $240\text{ }^{\circ}\text{C}$). A ROSAND[®] RH2000 capillary rheometer with two dies was used for these measurements. The first die ($\varnothing 1\text{ mm}$) was used in the shear range from 10^{-1} to 20 s^{-1} shear rate while the second die ($\varnothing 2$

mm) was used in the shear rate range 20 to $2 \cdot 10^4 \text{ s}^{-1}$. For example, the shear viscosity versus the shear rate for the neat PP and the fourth PP/MWCNT composites at 200 °C, are reputed in Figure 5. Similarly, the test temperature influence on the shear viscosity is shown in the Figure 6 for the 4 wt% PP/MWCNT composite. One can notice that the same pattern of results is identifiable to the other temperatures and the other composites (neat PP and 1, 2 and 8 wt% PP/MWCNT composites). Finally, the shear viscosity versus the temperature for the neat PP and the fourth PP/MWCNT composites at fixed shear rate ($\dot{\gamma} = 200 \text{ /s}$) are reputed in Figure 7. This fixed value of the shear rate corresponds to an average shear rate of the mixing phase.

At fixed temperature, the shear viscosity of the neat PP and PP/MWCNT composites decreases with the increase of the shear rate. These viscosity curves clearly indicate the significant effect of the MWCNTs content. When the shear rate is in the range $10^{-1} - 10^2 \text{ s}^{-1}$, the PP/MWCNT composite exhibit a shear thinning effect whereas the neat PP exhibits only small shear rate dependence, revealing a Newtonian plateau. However, from 1 wt% MWCNT content, the viscosity curves present a much steeper slope at low shear rate, and there is no Newtonian plateau within the shear rate range studied. Also, from 4 wt% MWCNT, the viscosity curves appear nearly power law over this range of shear rate. This phenomenon is related to the fact that, the MWCNTs – MWCNTs interactions begin to dominate as the MWCNTs content increases, eventually leading to a percolation and a formation of interconnected MWCNT structures. One can mention Girish et al. [14] and Gu et al. [15] who have reported that the shear viscosity of the confined polymer melts is greater than that of bulk chains. Furthermore, at high MWCNTs content, MWCNTs will entangle together to form interconnected structures. Hence, it results that the flow of the PP/MWCNT composite decreases as it was also reported by Lee et al [16]. However, when the shear rate is in the range $10^2 - 2 \cdot 10^4 \text{ s}^{-1}$, the shear viscosity of the PP/MWCNT composite of the same order than the neat PP: the effect of the MWCNT content is less important than at low shear rates. When shear rate is increasing, the shear thinning effect is enhanced and the wall slip phenomena

occurring between PP/MWCNT and the wall of the rheometer is predominant, as it is supposed by Lee et al. [17] and Lam et al. [18].

Finally for one PP/MWCNT composite shade, the viscosity curves indicate a decrease of the shear viscosity with the increase of the temperature. This is due to the fact that the shear viscosity of the polypropylene decreases when heating.

3.2. Characterization of the shear viscosity for PP/MWCNT composites

The previous investigations on the rheological behavior of the neat PP and the fourth PP/MWCNT composites clearly show an high dependence of the shear viscosity on the shear rate and the temperature. Thus, the constitutive model must be able to predict the flow of composites under various processing conditions and particularly the shear rate and the temperature. Most of the material flow models that take into account the shear rate and the temperature effects are summarized in Carreau et al [19]. One can mention the power law model, but it does not model the Newtonian plateau at low shear rates. A more convenient model proposed by Cross [20] allows switching from the Newtonian plateau at low shear rates to a straight line at high shear rates. However, this transition leads to a slope break that the model does not adjust. Carreau [4] proposed a model to modify the slope break by changing the Cross law without adding additional parameters. This Carreau law expression is :

$$\mu(\dot{\gamma}, T) = \mu_0(T) \left(1 + (\lambda \dot{\gamma})^2 \right)^{\frac{n-1}{2}} \quad (1)$$

where $\mu(\dot{\gamma}, T)$ is the shear viscosity, T the temperature and $\dot{\gamma}$ the equivalent shear rate defined by:

$$\dot{\gamma} = \sqrt{\frac{2}{3} dev(\underline{\dot{\epsilon}}) : dev(\underline{\dot{\epsilon}})} \quad (2)$$

with $\underline{\dot{\epsilon}}$, defined as the shear rate tensor versus the velocity field $\vec{V}$:

$$\underline{\dot{\epsilon}} = \frac{1}{2} \left(\underline{grad}(\vec{V}) + \underline{grad}^t(\vec{V}) \right). \quad (3)$$

and $dev(\underline{\dot{\epsilon}})$, the deviatoric part of the shear rate tensor:

$$dev(\underline{\dot{\epsilon}}) = \underline{\dot{\epsilon}} - \frac{1}{3} Tr(\underline{\dot{\epsilon}}) \underline{I} \quad (4)$$

where $\underline{I}$ is the second order identity tensor. The index n is typically called the shear thinning index. The term $\mu_0(T)$ is identified as the material consistency and it is a characteristic relaxation time of the material.

In this case, the following expression for the material consistency is proposed:

$$\mu_0(T) = \mu_0 e^{-bT} \quad (5)$$

where b is another characteristic time of the material. With this suggested constitutive model, thermal effects are accounted and the transition from the power law to the Newtonian plateau is more suitable.

The rheological parameters (μ_0 , b , λ and n) are summarized in table 1 for the neat PP and each PP/MWCNT composite. One can notice that the parameter μ_0 increases with MWCNTs content while the shear thinning index n substantially decreases. For the PP/MWCNT composites with 4 and 8 wt% MWCNTs content, the parameter μ_0 is higher than for other contents. In these conditions, the constitutive model identified for the Carreau law enriched temperature is almost equivalent to the power law model. Comparison between the experimental datas and the identified Carreau law for the neat PP and each PP/MWCNT composite is related in Figure 8. One can notice a good correlation between experimental and continuous datas.

4. Numerical simulation of the PP/MWCNT flow in the twin screw mixer

4.1. Problem formulation

This work aims at predicting the material (the neat PP and PP/MWCNT composites) flow into the Brabender[®] mixer during the mixing phase. Many assumptions must be considered to lead these numerical simulations. First of all, a two dimensional (2D) problem is considered

as an approximation of the section screw. In addition, one considers a laminar and incompressible flow without volumic loads and the material behavior follows the constitutive Carreau law proposed in the previous section.

In order to account the rotating motion of both screws, the material domain Ω is divided into three sub-domains described in Figure 9 as:

- Ω_1 , with fixed frame $R_I: (\vec{x}_1, \vec{y}_1, \vec{z}_1)$,
- Ω_2 , around the left screw with clockwise moving mesh, $R_2: (\vec{x}_2, \vec{y}_2, \vec{z}_2)$,
- Ω_3 , around the right screw with counterclockwise moving mesh, $R_3: (\vec{x}_3, \vec{y}_3, \vec{z}_3)$.

Thus, an Arbitrary Lagrangian – Eulerian (ALE) method with moving mesh on both Ω_2 and Ω_3 sub-domains is used to formulate the problem.

By considering the above geometrical definitions, the resolution 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 – Stockes equations:

$$\left. \begin{aligned} \text{div} \vec{V} &= 0 \\ \rho \frac{d\vec{V}}{dt} &= -\overrightarrow{\text{grad}}(p) + \mu(\dot{\gamma}, T) \vec{\Delta}(\vec{V}) \end{aligned} \right\} \text{ into } \Omega_1 \cup \Omega_2 \cup \Omega_3 \quad (6)$$

$$\quad (7)$$

where $\vec{\Delta}$ is the laplacian operator.

The temperature evolution is governed by the heat equation, given by the equation (8):

$$\rho C_p \left\{ \frac{\partial T}{\partial t} + \overrightarrow{\text{grad}}(T) \cdot \vec{V} \right\} + \text{div}(\vec{q}) = 2\mu(\dot{\gamma}, T) \dot{\underline{\underline{\epsilon}}} : \dot{\underline{\underline{\epsilon}}} \quad \text{into } \Omega_1 \cup \Omega_2 \cup \Omega_3 \quad (8)$$

where C_p is the specific heat coefficient. The Fourier's law gives the relation between the heat flow $\vec{q}$ and the temperature T :

$$\vec{q} = -K \cdot \overrightarrow{\text{grad}}(T) \quad (9)$$

where K is the thermal conduction coefficient. Assuming this relation, the heat equation becomes:

$$\rho C_p \left\{ \frac{\partial T}{\partial t} + \overrightarrow{grad}(T) \cdot \vec{V} \right\} - K \Delta T = 2\mu(\dot{\gamma}, T) \dot{\underline{\underline{\epsilon}}} : \dot{\underline{\underline{\epsilon}}} \quad \text{into } \Omega_1 \cup \Omega_2 \cup \Omega_3 \quad (10)$$

The density ρ is given by the well-known mixture rule:

$$\rho = \left(\frac{f}{\rho_c} + \frac{1-f}{\rho_p} \right)^{-1} \quad (11)$$

The modeling of the thermal conduction into polypropylene/nanotubes composite is not obvious, due to the thermal anisotropy of nanotubes and their random orientation into the polypropylene. The orientation of the nanotubes is sensitive to the processing method. Typically, the measured thermal conduction coefficient in the axes of the nanotubes is higher than that measured in the transverse direction. In this study, the model issued from Hamilton et al. [21] is used to evaluate the conduction coefficient:

$$K = K_p \frac{\alpha + (n-1) - (n-1)(1-\alpha)f_v}{\alpha + (n-1) + (1-\alpha)f_v} \quad (12)$$

where K_p is the polymer conduction coefficient ($n \approx 6$ for cylindrical particles), f_v the volume fraction of nanotubes and α an undimensional coefficient defined by:

$$\alpha = \frac{K_c}{K_p} \quad (13)$$

Where K_c is the nanotubes conduction coefficient. A similar relation can be written for the composite specific heat C_p :

$$C_p = C_{PP} \frac{\alpha + (n-1) - (n-1)(1-\beta)f_v}{\alpha + (n-1) + (1-\beta)f_v} \quad (14)$$

where C_{PP} is the polymer specific heat and β an undimensional coefficient defined as:

$$\beta = \frac{C_{pc}}{C_{PP}} \quad (15)$$

where C_{pc} is the nanotubes specific heat. Average measured values of the conduction coefficient and the specific heat for the nanotubes provided by Fuji et al. [22] are used here

and an assessment of the different coefficients is given in the table 2 in addition to these given in the table 1.

Moreover, boundary conditions must be considered for the simulations. For our problem, one can find these following conditions for both fluid and thermal problem:

- 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 : $\underline{\sigma} = 0$ on $\partial_4\Omega$,
- imposed temperature on the screws and the frame : $T = 473$ K on $\partial_1\Omega \cup \partial_2\Omega \cup \partial_3\Omega$,
- external heat transfer at the mixer inlet : $-K \overrightarrow{grad}(T) = h(T - T_{ext})\vec{n}$ on $\partial_4\Omega$,

where, $\underline{\sigma}$ is the stress tensor defined versus the pressure p , the shear viscosity $\mu(\dot{\gamma}, T)$ and the shear rate tensor $\underline{\dot{\epsilon}}$:

$$\underline{\sigma} = -p\underline{I} + 2\mu(\dot{\gamma}, T)\underline{\dot{\epsilon}} \quad (16)$$

T_{ext} is the external temperature fixed at 293 K, $\vec{n}$ stands for the outgoing normal vector and h the effective convection coefficient.

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:

$$\underline{\sigma}_1 - \underline{\sigma}_2 = 0 \text{ on } \partial_{12}\Omega \quad (17)$$

$$\underline{\sigma}_1 - \underline{\sigma}_3 = 0 \text{ on } \partial_{13}\Omega \quad (18)$$

for the fluid problem, and:

$$(\vec{q}_1 - \vec{q}_2)\vec{n}_{12} = 0 \text{ on } \partial_{12}\Omega \quad (19)$$

$$(\vec{q}_1 - \vec{q}_3)\vec{n}_{13} = 0 \text{ on } \partial_{13}\Omega \quad (20)$$

for the thermal problem.

Due to the time dependent problem statement, the following initial conditions are accounted:

$$\vec{V}(t=0) = \vec{0} \quad (21)$$

$$p(t=0) = 0 \quad (22)$$

$$T(t=0) = T_0 \quad (23)$$

Where T_0 is fixed to 423 °K, not far from the polypropylene melting temperature.

In order to complete this problem formulation, moving frames equations are given below. Let us consider M_2 and M_3 , two points of Ω_2 and Ω_3 , respectively. Moving frames equations impose the following relations:

$$\overrightarrow{O_2 M_2}(t) = r \cos\left(\frac{\pi N}{30} t\right) \overrightarrow{x_2} + r \sin\left(\frac{\pi N}{30} t\right) \overrightarrow{y_2} \quad \text{into } \Omega_2 \quad (24)$$

$$\overrightarrow{O_3 M_3}(t) = r \cos\left(\frac{\pi N}{30} t\right) \overrightarrow{x_3} - r \sin\left(\frac{\pi N}{30} t\right) \overrightarrow{y_3} \quad \text{into } \Omega_3 \quad (25)$$

where r is the effective distance between O_i and M_i and N the rotation speed fixed to 60 rpm.

4.2. Material and process numerical implementation

Comsol[®] is a modeling package for the simulation of any physical process and can be described with partial differential equations (PDEs). It proposes state-of-the art solvers that address quickly and accurately complex problems, while its intuitive structure is designed to provide flexibility and easy way to use. The constitutive fluid – thermal model has been implemented and can be assimilated to a multiphysic coupled problem between the “fluid flow module” (for the fluid problem), the “heat transfer module” (for the thermal problem) and the “ALE moving mesh module” (for the moving meshes).

The use of an automatic mesher, allows to discretized the sub-domains Ω_1 , Ω_2 and Ω_3 with 1066 quadratic TRI6 elements, resulting in a total of 9336 degrees of freedom (DOF). An explicit time stepping scheme is used for the time dependant solver algorithm with an automatic time step adjustment. A convergence test, which is not detailed here validates this mesh choice. The diagram related in Figure 11 shows the interaction between the three modules. The solution is given on the actual frames at each time step until $t = t_f$, where t_f designed the simulation time. One considers here that $t_f = 3s$.

4.3. Results

Many simulations were leaded for the neat PP and the fourth PP/MWCNT composites considering the rheological and the thermal parameters related in the table 1 and the table 2 respectively.

The following results are related to the PP/MWCNT composite with 8 wt% MWCNTs content. The same results tendencies are obtained for the other PP/MWCNT contents and the neat PP.

Figures 12(a), to 12(f) relate the velocity field at different time steps. One can notice that the maximum value for the velocity field is located at the middle of the frame ($x = 0.02$ m, $y = 0$) and near the screws extremity. Further, the wall adherence condition on the frame ($\vec{v} = \vec{0}$) is clearly respected.

The shear rate is represented in Figures 13(a) to 13(d), at $t = 1$ s and $t = 3$ s. These figures reveal that the shear rate is approximately constant in the cavity except near the screws extremity where the shear rate is nearly fifty times 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.

The temperature evolution is shown in Figures 14(a) to 14(f). 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 ($T = 473$ °K). During the simulation, the temperature in the cavity increases to a limit value equal to 473 °K, corresponding to the imposed mixing temperature on the frame and screws walls. This simulation clearly indicates that the mixing temperature is quickly reached, which guarantees optimal mixing conditions. The heat transfer influence at the mixer inlet is shown in these figures. This shows that a significant variation of the temperature in the middle of the cavity, where the temperature is practically equal to the PP melting temperature.

From the FEM analysis results, the resulting torque on both screws can be calculated for each PP/MWCNT composite and neat PP flow simulation. For example, let us consider the left screw mixing torque $\vec{C}$ expression is given by the following equations:

$$\vec{C} = \int_S \overrightarrow{O_2 P_2} \wedge \underline{\sigma}(\vec{n}) dS \quad (26)$$

where P_2 stands for a geometrical point of the screw boundary, $\vec{n}$ represents the outpointing normal vector at the screw/fluid boundary and S the lateral surface screw. Due to the 2D assumption, one can write the mixing torque per unit length $\vec{C}_l$ as:

$$\vec{C}_l = L \cdot \int_l \overrightarrow{O_2 P_2} \wedge \underline{\sigma}(\vec{n}) dl \quad (27)$$

where l is screw section perimeter, dl its curvilinear abscissa and L the screw length in the $(0_2, \vec{z}_2)$ axis direction. Assuming the definition of the stress tensor related in eq. (16), one can get explicitly the stress tensor components:

$$\underline{\sigma} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & 0 \\ \sigma_{12} & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix} \quad (28)$$

where:

$$\sigma_{11} = -p + 2\mu(\dot{\gamma}, T) \frac{\partial V_x}{\partial x} \quad (29)$$

$$\sigma_{22} = -p + 2\mu(\dot{\gamma}, T) \frac{\partial V_y}{\partial y} \quad (30)$$

$$\sigma_{12} = \mu(\dot{\gamma}, T) \left(\frac{\partial V_x}{\partial y} + \frac{\partial V_y}{\partial x} \right) \quad (31)$$

$$\sigma_{33} = -p \quad (32)$$

Assuming the following definitions for $\overrightarrow{O_2 P_2}$ and the outgoing $\vec{n}$ vectors:

$$\overrightarrow{O_2 P_2} = x \cdot \vec{x}_2 + y \cdot \vec{y}_2 \quad (33)$$

$$\vec{n} = n_x \cdot \vec{x}_2 + n_y \cdot \vec{y}_2 \quad (34)$$

The resulting mixing torque expression is given by:

$$\vec{C} = L \cdot \int_l [x(n_x \sigma_{12} + n_y \sigma_{22}) - y(n_x \sigma_{11} + n_y \sigma_{22})] dl \cdot \vec{z}_2 \quad (35)$$

Thus, a numerical integration of the eq. (35) is performed on the section screw perimeter, at each time step for each PP/MWCNT composite and the neat PP. Assuming that the screw length is about 47 mm, the mixing torque $\bar{C}$ can be calculated and thus represented in Figure 15.

Figure 15 shows that the torque increases with the MWCNT content. One can explain it due to the increase of the shear viscosity of the PP/MWCNT composite with the MWCNT content. Nevertheless, there is a more important gap between the 4 wt% and 8 wt% MWCNT content curves than the other ones.

Due to the temperature increase in the cavity, the shear viscosity decreases. Consequently, it results a decrease of the mixing torque versus time when for each PP/MWCNT composite. However, this decrease phenomenon is more significant when the MWCNT content increases. Finally, even if many assumptions are done, these numerical results are in good agreement with the experimental torque values, reported in Figure 4.

Conclusion

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 properly identified material behavior and an appropriate finite element modeling of the composite flow in a twin-screw mixer.

The first part of the paper relates the experiments carried out for the determination of the rheological properties of PP/MWCNT with various MWCNT contents estimated in the temperature range from 180 to 240 °C. The rheological properties have been in the range 10^{-1} to $2 \cdot 10^4 \text{ s}^{-1}$ using capillary rheometry. The significant effects of the MWCNT content have been proved, as the increase of shear viscosity versus MWCNT volumic fraction associated to shear rate increase. These rheological characterizations have been used to set up and to build a constitutive model for the flow of PP/MWCNT based on the extension of the well known Carreau law coupled with a thermal factor. The resulting parameters have been identified for the neat PP and the PP/MWCNT composites.

Then, physical and mechanical analyses have been proposed for the flows in a twin screw mixer, resulting in a finite element modeling of the mixing process; accounting the very high values of shear rate between the screw and the frame, as well as temperature contours. The compromise between experimental mixing torques and the ones obtained through the finite element simulations attests about the validity of the rheological flow model as well as the finite element results. The reported finite element simulations permit to account the temperature effects 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.

References

1. S. Iijima. Helical microtubes of graphitic carbon. *Nature*, 1991, 354(6348), 56-8.
2. N. Coleman, U. Kahn, W. J. Blau, Y.K. Gun'ko. Small but strong: A review of the mechanical properties of carbon nanotube-polymer composites. *Carbon*, 2006, 44, 1644-1652.
3. O. Breuer, U. Sundaraj. Big returns from small fibers: a review of polymer/carbon nanotube composites. 2004, *Polymer Composites*, 25, 630-645.
4. P.J. Carreau. Rheological equations from molecular network theories. *Trans. Soc. Rheol.*, 1972, 16(99-127).
5. S.L. Ruan, P. Gao, X.G. Yang, T.X. Yu. Toughening high performance ultrahigh molecular weight polyethylene using multiwalled carbon nanotubes. *Polymer*, 2003, 44(19):5643-54.
6. L. Jin, C. Bower, O. Zhou. Alignment of carbon nanotubes in a polymer matrix by mechanical stretching. *Appl. Phys. Lett.*, 1998, 73(9):1197-9.
7. M.S.P. Shaffer, A.H. Windle. Fabrication and characterization of carbon nanotube/poly(vinyl alcohol) composites. *Adv. Mater.*, 1999, 11(11):937-41.
8. D. Qian, E.C. Dickey, R. Andrews, T. Rantell. Load transfer and deformation mechanisms in carbon nanotube-polystyrene composites. *Appl. Phys. Lett.*, 2000, 76(20):2868-70.

9. Z. Jin, K. Pramoda, G. Xu, S.H. Goh. Dynamic mechanical behavior of melt-processed multi-walled carbon nanotube/poly(methyl methacrylate) composites. *Chem. Phys. Lett.*, 2001, 337(1–3):43–7.
10. R. Andrews, D. Jacques, D.L. Qian, T. Rantell. Multiwall carbon nanotubes: synthesis and application. *Acc. Chem. Res.*, 2002, 35(12): 1008–17.
11. P. Pötschke, A.R. Bhattacharyya, A. Janke, H. Goering. Melt mixing of polycarbonate/multi-wall carbon nanotube composites. *Compos. Interf.*, 2003, 10(4–5):389–404.
12. C.C. Teng, C.C.M. Ma, Y.W. Huang, S.M. Yuen, C.C. Weng C.H. Chen, S.F. Su. Effect of MWCNT content on rheological and dynamic mechanical properties of multiwalled carbon nanotube/polypropylene composites. *Composites Part A: Applied Science and Manufacturing*, 2008, 39(1869-1875).
13. M.K. Seo, S.J. Park. Electrical resistivity and rheological behaviors of carbon nanotubes-filled polypropylene composites. *Chem. Phys. Lett.*, 2004, 395(44-48).
14. G. Girish, C. Ramesh, A. Lele. A rheological study on the kinetics of hybrid formation in polypropylene nanocomposites. *Macromolecules*, 2001, 34(852–8).
15. S.Y. Gu, J. Ren, Q.F. Wang. Rheology of poly(propylene)/clay nanocomposites. *J. Appl. Polym. Sci.*, 2004, 91(2427–34).
16. K. Lee, M.R. Mackley. The significance of slip in matching polyethylene processing data with numerical simulation. *J. Non-Newton Fluid*, 2000, 94(159–77).
17. S.H. Lee, M.W. Kim, S.H. Kim, J.R. Youn. Rheological and electrical properties of polypropylene/MWCNT composites prepared with MWCNT masterbatch chips. *Eur. Polym. J.*, 2008, 44(1620–1630).
18. Y.C. Lam, Z.Y. Wang, S.C. Joshi. Wall slip of concentrated suspension in capillary flows. *Powder Technology*, 2007, 177(162–169).
19. P.J. Carreau, D.C.R. De Kee, O.R.P. Chhabra. *Rheology of polymeric systems : principles and applications*. Hanser, Munich, 1997.

20. M.M. Cross. Rheology of non-newtoian fluids: a new flow equation for pseudoplastic systems. J. Colloid Sci., 1965, 20(417-437).
21. R. L. Hamilton, O. K. Crosser. Thermal Conductivity of Heterogeneous Two-Component Systems. Ind. et Engin. Chem. Fund., 1962, (1-187).
22. M. Fujii, X. Zhang, H. Xie, H. Ago, K. Takahashi, T. Ikuta, H. Abe, T. Shimizu. Measuring the Thermal Conductivity of a Single Carbon Nanotube. Phys. Rev. Lett., 2005, 95,065502.

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Table 1: Rheological parameters for the neat PP and each PP/MWCNT composite.

MWCNT content	0 wt%	1 wt%	2 wt%	4 wt%	8 wt%
μ_0 (Pa·s ⁿ)	20778	34214	172783	$2 \cdot 10^6$	$2 \cdot 10^7$
b (°C ⁻¹)	0.0155	0.0116	0.0148	0.0206	0.0242
λ (s ⁻¹)	0.207	0.514	0.942	2.645	2.733
n	0.4	0.34	0.29	0.27	0.25

Table 2: Thermal parameters for the neat PP and each PP/MWCNT composite.

MWCNT content	0 wt%	1 wt%	2 wt%	4 wt%	8 wt%
ρ (g·cm ⁻³)	0.900	0.903	0.906	0.911	0.923
C_p (J·kg ⁻¹)	1800	1837	1874	1949	2096
K (W·m ⁻¹ ·kg ⁻¹)	0.200	0.204	0.208	0.217	0.233

Fig. 1: As-received MWCNTs SEM microphotography.

Fig. 2 : The Brabender® mixer EC W50EHT .

Fig. 3: Mixing cavities and twin screw mixer.

Fig. 4 : Mixing torque vs time for the neat PP and the composites (PP/MWCNT 1, 2, 4 and 8 wt%)

Fig. 1 : Shear viscosity versus shear rate at 200 °C for the neat PP and the loaded composites.

Fig. 1 : Shear viscosity versus shear rate at 180, 200, 220 and 240 °C for the 4 wt% PP/MWCNT composite.

Fig. 1 : Shear viscosity versus temperature for the neat PP and the loaded composites (fixed shear rate)

Fig. 1 : Shear viscosity as a function of the shear rate at 180, 200, 220 and 240 °C for the 4 wt% PP/MWCNT composite : experimental datas and Carreau law enriched temperature fitting curves.

Fig. 9 : Moving and fixed frame, sub domains and boundaries definition.

Fig. 10 : Mesh definition related to the two screws mixer FE model (9336 DOF).

Fig. 1 : Interactions diagram between “material flow”, “heat transfer” and “moving mesh module”.

Fig. 12 : Velocity fields (in mm/s) at several time steps for the 8wt% PP/MWCNT composite.

Fig. 13 : Shear rate (in /s) at $t = 1 \text{ s}$ and $t = 3 \text{ s}$ for the PP/MWCNT composite with 8 wt% in MWCNT.

Fig. 14: Temperature field (in K) at several time step for the PP/MWCNT composite with 8 wt% in MWCNT.

Fig. 15 : Mixing torque on the left screw for the neat PP and the fourth PP/MWCNT composites.