

# Simulation of the Reactive Rotational Molding Using Smoothed Particle Hydrodynamics

A. Hamidi, S. Khelladi, L. Illoul, A. Tcharkhtchi

**Abstract**—Reactive rotational molding (RRM) is a process to manufacture hollow plastic parts with reactive material has several advantages compared to conventional roto molding of thermoplastic powders: process cycle time is shorter; raw material is less expensive because polymerization occurs during processing and high-performance polymers may be used such as thermosets, thermoplastics or blends. However, several phenomena occur during this process which makes the optimization of the process quite complex. In this study, we have used a mixture of isocyanate and polyol as a reactive system. The chemical transformation of this system to polyurethane has been studied by thermal analysis and rheology tests. Thanks to these results of the curing process and rheological measurements, the kinetic and rheokinetic of polyurethane was identified. Smoothed Particle Hydrodynamics, a Lagrangian meshless method, was chosen to simulate reactive fluid flow in 2 and 3D configurations of the polyurethane during the process taking into account the chemical, and chemiorehological results obtained experimentally in this study.

**Keywords**—Reactive rotational molding, free surface flows, simulation, smoothed particle hydrodynamics, surface tension.

## I. INTRODUCTION

THE complexity of the flow during process, as well as the large number of parameters and interrelated variables affecting the flow, make the RRM process difficult to understand, describe, control and optimize. Besides the process kinetics, other important elements in the process modeling are the material flow taking into account chemiorheological, surface tension, and viscoelastic behavior. The optimization of RRM of such system requires the analysis of the structure evolution. During gelation, an infinite three-dimensional network is formed and accompanied by an increase in viscosity due to the increase of molar weights. The gel point marks the limit of the processing. In the case of the RRM, the shape of the part should be formed before gelation. An optimal interval of viscosity should be reached before the gel point. Although the gelation is controlled by the reaction between the largest reduced mobility clusters, the pre-gel is characterized by the formation of low molecular weight oligomers.

This work deals with rheological, thermal analysis of polymerization kinetics of thermoset polyurethane with a different rate of heating. In the second part, the prediction of fluid flow was investigated using Smoothed Particle

Hydrodynamics method. This simulation involves the rheokinetic in dynamic conditions and the implementation of surface tension force.

## II. KINETIC AND RHEOKINETIK MODELING

The knowledge of kinetic parameters of reactive thermoset polyurethane is essential in the design and processing of polymer technology. Kinetic prediction of the cure pattern in dynamic conditions is very interesting.

Polyurethane thermoset studied here is produced by the polyaddition of a polyisocyanate and a polyol in the presence of a catalyst, and the reaction process is governed by the high reactivity of isocyanate group [1]. The mechanism of the polymerization of polyurethane has been investigated in the literature, mostly to the classical second order reaction [2]-[4]. In this study, the reaction rate is controlled by a tin complex catalyst concentration and the kinetic law must integrate its effect. Sato's model [5] is appropriated to describe this kinetics:

$$\frac{d\alpha}{dt} = k_1([NCO]_0 - \alpha)([OH]_0 - \alpha)^2 + k_2\alpha([NCO]_0 - \alpha)([OH]_0 - \alpha) + k_3[cat]([NCO]_0 - \alpha)([OH]_0 - \alpha) \quad (1)$$

where  $\alpha$ =conversion,  $k_1$ ,  $k_2$ ,  $k_3$ =reaction constants,  $[NCO]_0$ ,  $[OH]_0$ ,  $[cat.]$ =initial concentrations in isocyanate, alcohol, and catalyst, respectively.

The rate of conversion is measured for non-isothermal runs and compared with results calculated from SATO model.

As a result of this reaction, the reactive system first increases in viscosity and eventually cross-links and become set, reaching gel point, and as a result, it can no longer flow or dissolve. Therefore, it is important to understand the rheological behavior of the thermosetting resin in order to optimize the operating conditions for a reactive polymer process that includes both reaction and viscous. In order to model a reactive polymer process, a viscosity function that can express the relationship between viscosity and temperature, shear rate and conversion is necessary. In this study, we used Castro and Macosko model which give relationship between the viscosity and conversion, as:

$$\eta = \eta_0 \left( \frac{\alpha_{gel}}{\alpha_{gel} - \alpha} \right)^{a+b\alpha} \quad (2)$$

where:  $\alpha_{gel}$  represents the conversion at gelation point, and  $\eta_0$ ,  $a$  and  $b$  are empirical constants.

A. Hamidi S. Khelladi, A. Iloul, A. Tcharkhtchi are with the Ecole Natioanle Superieure D'arts Et Metiers, PIMM Laboratory Paris, France (phone: +33 1 44 24 61 05, +33 1 44 24 63 91, +33 1 44 24 61 05, +33 1 44 24 63 01; e-mail: abdelmoumen.hamidi @ensam.eu, Sofiane.khelladi @ensam.eu, amran.illoul@ensam.eu, abbas.tcharkhtchi@ensam.eu).

### III. MATERIALS AND METHODS

#### A. Materials

The reactive materials, provided by Raigi (Arbouville, France), are two separate components for polyurethane synthesis. The first component is a polyol mixed with crosslinking agents and catalysts; the second one an isocyanate. The formulation was developed by Raigi for RRM applications.

#### B. Thermal Properties

The Differential Scanning Calorimetry is widely used to analyze the cure kinetics of thermosets. Linear heating runs are carried out in a TA instruments DSC Q10 thermal analyzer. Samples were prepared with approximately 10 mg of the mixture (polyol and isocyanate) in hermetic aluminum capsules. During the study the samples are heated from  $-50\text{ }^{\circ}\text{C}$  to  $200\text{ }^{\circ}\text{C}$  with a heating rate 2, 5, 7, 12, 15, and  $18\text{ }^{\circ}\text{C}/\text{min}$ .

#### B. Rheological Measurements

Rheological measurements of the polyurethane reactive mixtures were carried out an Ares Rheometer from TA Instruments equipped with 25 mm diameter parallel plates. Measurements are taken each 5 seconds, and the gap between parallel plates is between 0.5 and 1 mm wide.

### IV. EXPERIMENTAL RESULTS AND DISCUSSION

#### A. Kinetic Modelling

The advantage of this analysis is the description of the transformation of heating rate in function of time and temperature. Indeed, in the rotational molding process, the reactive material is subjected to high temperatures up ramps under certain conditions which can reach  $20\text{ }^{\circ}\text{C}/\text{min}$ . The dynamic analysis is more appropriate to describe the kinetic behavior of the systems studied. Here, the kinetics is studied by following the consumption of isocyanate function. Conversion is plotted as a function of temperature at different rates of heating. The DSC test results for a dynamic cure at different heating rates are represented in thermograms such as the one illustrated in Fig. 1. The shape of the thermograms shows two exothermic peaks major peak around  $140\text{ }^{\circ}\text{C}$  correspond to the crosslinking of polyurethane and the second peak represents secondary reaction due to the consumption of NCO by side reactions as the formation of allophanes [6].

An attempt was made to fit this experimental data to the Sato's model. Fig. 2 shows the experimental results and the numerical results for the reaction between isocyanates and polyols with the presence of a catalyst. A reasonable fit of the reaction profile could be achieved with Sato's model.

#### B. Thermal Properties

The Differential Scanning Calorimetry is widely used to analyze the cure kinetics of thermosets. Linear heating runs are carried out in a TA instruments DSC Q10 thermal analyzer. Samples were prepared with approximately 10 mg of the mixture (polyol and isocyanate) in hermetic aluminum

capsules. During the study the samples are heated from  $-50\text{ }^{\circ}\text{C}$  to  $200\text{ }^{\circ}\text{C}$  with a heating rate 2, 5, 7, 12, 15, and  $18\text{ }^{\circ}\text{C}/\text{min}$ .

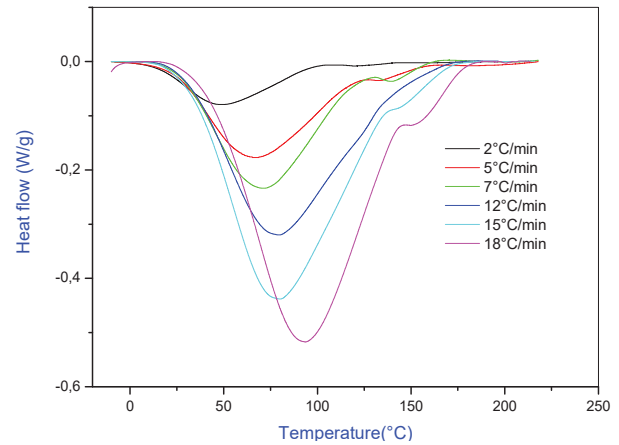


Fig. 1 Evolution of the heat flux with temperature for the non-isothermal scans

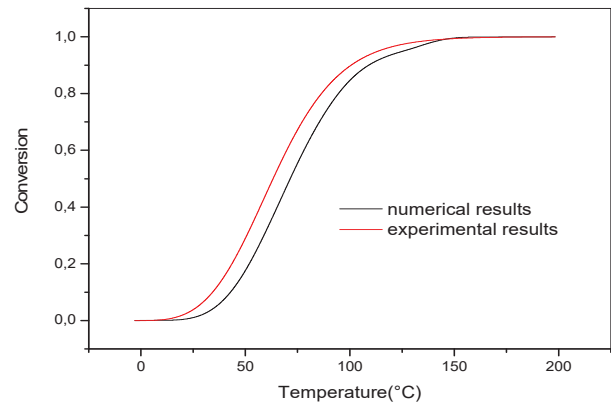


Fig. 2 Simulated (-) and experimental conversion (-) data versus temperature for  $7\text{ }^{\circ}\text{C}/\text{min}$

#### B. Rheological Measurements

The aim of this section is the determination of the law of evolution of viscosity for a Newtonian fluid. Therefore, rheological experiments were performed to assess the rheological properties of the polyurethane reacting system, called dynamic temperature ramp in order to determine the system's viscosity at a different rate of heating: 2, 5, 7, 12, 15 and  $18\text{ }^{\circ}\text{C}/\text{min}$ . The material's rheological properties are measured in multifrequency mode. Measurements are taken each 5 seconds, and the gap between parallel plates is between 0.5 and 1 mm wide.

Fig. 3 shows the evolution of the viscosity for  $7\text{ }^{\circ}\text{C}/\text{min}$  where  $\alpha_{gel} = 0.6$ . In order to correlate the kinetic model,  $\alpha$  and the experimental rheological results,  $\eta(t, T)$ , the Macko-Castro chemorheological model presented in (2) is used. As shown in the figure, the model describes successfully the evolution of viscosity. Parameters are determined through regression based on error minimization.

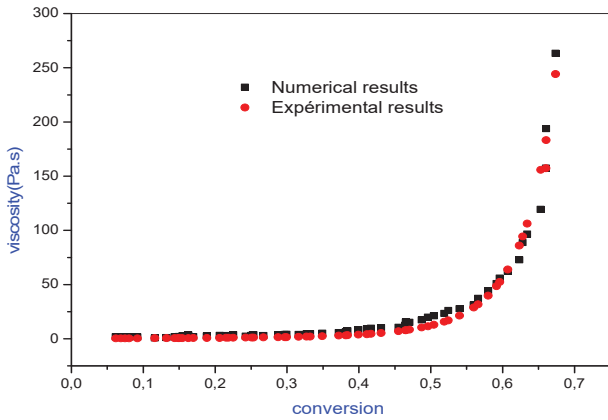


Fig. 3 Simulated (■) and experimental viscosity (●) data versus temperature for 7°C/min

### V. NUMERICAL MODEL: SMOOTHED PARTICLE HYDRODYNAMICS

The study of fluid flow is described by the Navier-Stokes equations that reflect the mass conservations, momentum, and total energy. A state equation is combined with these equations in order to describe the thermodynamic behavior of the fluid. In Lagrangian formalism this equation can be written as [7]:

$$\nabla \vec{v} = 0 \quad (2)$$

$$\frac{\partial \vec{v}}{\partial t} = g - \frac{1}{\rho} \nabla P + \frac{1}{\rho} \vec{f} \quad (3)$$

where  $g$ ,  $P$ ,  $v$ , and  $\rho$  represent the gravitational acceleration, pressure, the velocity vector and density, respectively.  $\vec{f}$  denotes the surface force which acts only at the interface only.

Among the methods that allow us to simulate the free-surface flow, there are meshless methods, in particular, Smoothed Particle Hydrodynamics method [8], [9]. The principle of the SPH method is based on field reconstruction from a cloud of discrete and disordered points.

This approximation in discrete notation permits to find the value of the scalar field  $A(r)$  at any point, at a particle  $a$ , the following equation is used:

$$A(r) = \sum_b \frac{m_b}{\rho_b} A_b W_{ab} \quad (4)$$

where the summation is over all the particles within the region of compact support of kernel function.  $a$  and  $b$  represent the SPH particles;  $m_b$  and  $\rho_b$  are mass and density of particle  $b$ , respectively.  $W_{ab}$  is weight or kernel function which has compact support.

In SPH, the fundamental principle is to approximate any function  $A(r)$  by:

$$A(r) = \int A(r') W(r - r', h) dr' \quad (5)$$

where:  $h$  is the smoothing length. In present simulation, the cubic spline kernel has been used:

$$W(r, h) = \alpha_D \begin{cases} 1 - \frac{3}{2}q^2 + \frac{3}{4}q^3 & 0 \leq q \leq 1 \\ \frac{1}{4}(2 - q)^3 & 1 \leq q \leq 2 \\ 0 & q \geq 2 \end{cases} \quad (6)$$

where  $q = r/h$ ,  $r$  is the distance between particle  $a$  and  $b$ .  $\alpha_D$  is  $10/(7\pi h^2)$  in 2D and  $1/(\pi h^3)$  in 3D. The Navier-Stokes equations are discretized by the SPH method for each particle, will be given below, the continuity equation (8), momentum equation (9) and thermal energy (10).

$$\frac{d\rho_a}{dt} = \sum_b m_b (\vec{v}_a - \vec{v}_b) \cdot \vec{\nabla} W_{ab} \quad (7)$$

where:  $\rho_a, v_a$  are density and velocity of particle  $a$ , respectively;  $m_b$  and  $v_b$  are mass and velocity of particle  $b$ .

$$\frac{d\vec{v}_a}{dt} = - \sum_b m_b \left( \frac{P_a}{\rho_a^2} + \frac{P_b}{\rho_b^2} \right) \vec{\nabla} W_{ab} + \sum_b \frac{m_b (\eta_a + \eta_b) v_{ab}}{\rho_a \rho_b} \left( \frac{1}{r_{ab}} \frac{\partial W_{ab}}{\partial r_a} \right) + \vec{g} + \vec{f} \quad (8)$$

where:  $P_a, P_b$  and  $\eta_a, \eta_b$  are pressure and viscosity of particles  $a$  and  $b$ , respectively and  $\vec{g}$  represents gravity. And  $\vec{f}$ : surface tension surface and is given by:

$$\vec{f} = \sigma k \vec{n} \delta_s \quad (9)$$

where  $\sigma$ : coefficient of surface tension;  $k$ : the curvature;  $\vec{n}$ : normal vector of surface;  $\delta_s$ : surface delta function and it's equal to  $1/\epsilon$  where:  $\epsilon$  represents particle spacing.

$$\frac{dE_a}{dt} = \sum_b \frac{4m_b}{\rho_a \rho_b} \frac{k_a k_b}{k_a + k_b} T_{ab} \frac{r_{ab} \cdot \nabla_a W_{ab}}{r_{ab}^2 + \epsilon^2} \quad (10)$$

where  $k_a$  and  $k_b$  are respectively the conductivity of particle  $a$  and  $b$ ,  $T_{ab}$  is the difference between temperatures of particles  $a$  and  $b$ . This equation involves an explicit conductivity which can be variable. This allows simulating heat transfer of multiple materials with different conductivities.

To describe the thermodynamic behavior of the fluid, we have associated with this system an equation of state which shows the variation pressure  $P$  in function of density  $\rho$ .

$$P = P_0 \left[ \left( \frac{\rho}{\rho_0} \right)^\gamma - 1 \right] \quad (11)$$

where:  $P_0$  is the magnitude of the pressure and  $\rho_0$  is the reference density.  $P_0$  is given by:

$$P_0 = \frac{c_s^2 \rho_0}{\gamma} \quad (12)$$

with  $c_s$  is speed sound at the reference density and  $\gamma$  is a problem dependent parameter-isocyanate. The formulation was developed by Raigi for RRM applications.

#### B. Treatment of Boundary Conditions

In this study, we used approach, proposed by Monaghan by employing repulsive force method where the wall is described by particles which exert a short-range repulsive force similar to a Leonard-Jones potential force on fluid particles. With this

kind of force, only one layer of particles is placed on the wall with identical mass and density to inner particles. Nevertheless, the boundary conditions adopted in our study produce no-slip conditions. In this configuration, fluid particles cannot adhere to the boundary particles (except for very low velocities). To simulate the adhesion of RRM on the mold surface, we used the model to fix the fluid particles when they reached a certain viscosity, and they are exposed to a certain distance from the mold during a certain time [10].

### B. Surface Tension Model

To implement force tension surface in SPH solver, the interface between polymer and air is dynamically tracked by finding all the particles of interface air-polymer. First, the boundary particles are detected by free-surface detection algorithm developed by Bascasco, Terissa, and NAA [11], [12] in two and three dimensions. Then, we reconstructed locally the interface by fitting circle [13] and fitting sphere method [14], in two and three-dimensional configurations, respectively.

## VI. NUMERICAL RESULTS

We applied our algorithm to simulate 2D flows in a cylinder mold geometry rotating around its main axis. Approximately 20000 particles are necessary to build the mold and the fluid. The mold temperature is 80 °C and the initial fluid temperature 25 °C. The rotation speed of the axis is 7.5 rpm. We simulate the flows occurring during rotation with rheokinetic model Mcko-Casto obtained in this experiment. We simulate the flows occurring during rotation with or without tension surface to show the effect of this force on the quality of final parts.

For the simulations occurred with surface tension force, the internal surface represents less roughness than the simulation which did not take into consideration the effect of surface tension. As we know, surface tension is caused by cohesive forces between the liquid's molecules. Inside the reactive fluid, each molecule is pushed and pulled equally in every direction by nearby molecules. The net force acting on these molecules is zero. The molecules at the surface, however, do not have molecules on all sides. This results in a net force pointing inwards into the liquid. This creates internal pressure and forces the liquid surface to contract to the smallest possible area which permits the increasing of the curvature in the internal surface of the part.

Like to the two-dimensional simulations, we conducted the numerical study with simple mold geometry; cylindrical mold shape has a length of 20 cm and a diameter of 10 cm. The initial spacing particle is 2 mm which corresponds to 4 mm in the final part. The mold is represented by 20000 solid particles, and its temperature is set at 80 °C. The polymer which is polyurethane is represented by 90000 of fluid particles; the initial temperature is set at 25 °C (Fig. 5). The evolution of viscosity follows the same law which is used in two-dimensional configurations.

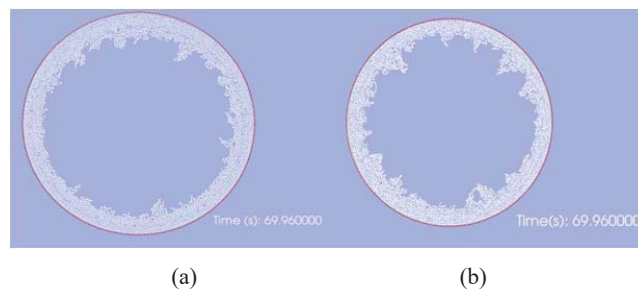


Fig. 4 The effect of surface tension force in the roughness of the internal surface of (a) without tension surface (b) with tension force

The fluid flow and heat transfer are shown in the below figure. Once the three conditions of adhesion model are satisfied, the reactive starts to adhere to the internal surface of the mold. When viscosity increases, the flow is slower and smoother; we can observe more material cohesion. Moreover, the fluid seems to stick to the mold surface.

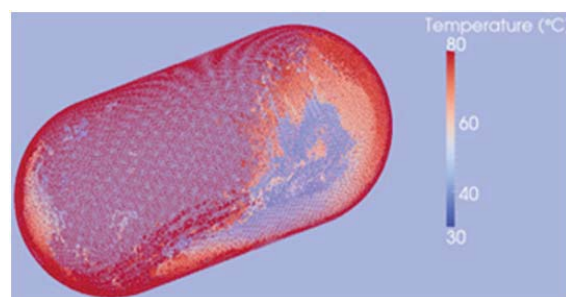


Fig. 5 3D cylinder mold

## VII. CONCLUSION

In this paper, we have studied the reactive thermoset polyurethane flow during RRM taking into account all transitions and physical phenomena occurring during the process: kinetic, chemiorheological, and surface tension effect. The combination of thermal and rheological results obtained in this study permit to define the relationship between viscosity and conversion and the chemo-rheological model for this polyurethane has been developed and implemented in the simulation of fluid flow.

The implementation of surface tension has improved the quality of our simulations by reducing the roughness of the internal surface. To enhance our solver, we will incorporate new criterion in the adhesion model, and we also take account of the non-Newtonian character of the polymer using viscoelastic models describing the behavior of our material during the process.

## REFERENCES

- [1] C. Hepburn, "Polyurethane elastomers 2nd Edition," Elsevier Science Publishers LTD, 1992.
- [2] P. Król, "Generalization of kinetics in the reaction of isocyanates and polyols for modeling a process-yielding linear polyurethane, 1," Journal of Applied Polymer Science, vol. 57, pp. 739-749, 1995.
- [3] S. Boufi, M. N. Belgacem, J. Quillerou, and A. Gandini, "Urethanes and polyurethanes bearing furan moieties. 4. Synthesis, kinetics and characterization of linear polymers," *acromolecules* vol. 26, pp. 6706-6717, 2014/10/30 1993.

- [4] S. Farzaneh, S. Riviere, and A. Tcharkhtchi, "Rheokinetic of polyurethane crosslinking time-temperature-transformation diagram for rotational molding," *Journal of Applied Polymer Science*, vol. 125, pp. 1559-1566.
- [5] M. Sato, "The Rates of Reaction of 1-Alkenyl Isocyanates with Methanol," *Journal of the American Chemical Society*, vol. 82, pp. 3893-3897, 2014/10/30 1960.
- [6] C. Pavier and A. Gandini, "Urethanes and polyurethanes from oxypropylated sugar beet pulp: I. Kinetic study in solution," *European Polymer Journal*, vol. 36, pp. 1653-1658, 2000.
- [7] W. Dong, S. L. Jiang, X. Y. Huang, H. S. Liu, and Q. Q. Huang, "Investigation on the Non-Newtonian Fluid Flow in a Single Screw Extruder Using Incompressible SPH (ISPH)," *Advanced Materials Research*, vol. 482, pp. 745-748, 2012.
- [8] D. Violeau, *Fluid Mechanics and the SPH Method Theory and Applications*. Oxford: Oxford University express, 2012.
- [9] X. Xu, J. Ouyang, B. Yang, and Z. Liu, "SPH simulations of three-dimensional non-Newtonian free surface flows," *Computer Methods in Applied Mechanics and Engineering*, vol. 256, pp. 101-116, 2013.
- [10] S. Riviere, Khelladi, S., Farzaneh, S., Bakir, F., Tcharkhtchi, A., "Simulation of polymer flow using smoothed particle hydrodynamics method," *Polymer Engineering and Science*, vol. 53, pp. 2509-2518, 2013.
- [11] BarescasoA, TerissaH, NaaCF. Simple free-surface detection in two and three-dimensional SPH solver. 2013, arXiv:1309.4290
- [12] Terissa H, BarescasoA, Naa F. Three-Dimensional Smoothed Particle Hydrodynamics Simulation for Liquid Droplet with Surface Tension.2013,arXiv:1309.3868.
- [13] A. Hamidi, Khelladi, S., iloul, S., Tcharkhtchi, A., "Implementation of surface tension in polymer flow during Reactive Rotational Molding," in 9th SPHERIC International Workshop, Paris, FRANCE, 2012, pp. 87-94.
- [14] S. J. Ahn, W. Rauh, and H.-J. r. Warnecke, "Least-squares orthogonal distances fitting of the circle, sphere, ellipse, hyperbola, and parabola," *Pattern Recognition*, vol. 34, pp. 2283-2303, 2001.