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INFLUENCE OF HYDRODYNAMIC ACTIVATION ON A POLYMERIZATION REACTION IN A TAYLOR-COUETTE REACTOR

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Lucrarea este dedicată investigaţiilor experimentale asupra unei reacţii de polimerizare într-un reactor de tip Taylor-Couette (TCR). Scopul general al proiectului este studiul relaţiei dintre eficienţa de amestecare şi o reacţie chimică în TCR. Astfel, soluţii pre-amestecate de monomer-solvent sunt polimerizate in prezenta unui iniţiator de reacţie. În timpul reacţiei sunt extrase mostre care sunt apoi analizate din punct de vedere al proprietăţilor reologice, masei moleculare si conversiei. Pe baza datelor obţinute, se estimează domeniul parametrilor reologici în care modelul de caracterizare a eficienţei de amestecare este aplicabil.

The present work is concerned with experimental investigations on a polymerization reaction in a Taylor-Couette reactor (TCR). The overall aim of the project is to investigate the relationship between mixing and a chemical reaction in TCR. In this work premixed monomer-solvent solutions are polymerized in TCR in the presence of an initiator. Samples are extracted during the process and are characterized by means of rheological properties, molecular weight and conversion. As a result the rheological boundaries for which a previously investigated mixing model may be valid are estimated.

Keywords: Taylor-Couette flow, polymerization reactor

1. Introduction

Flow between concentric cylinders, with one or both cylinders rotating, also known as Taylor-Couette (TC) flow, is a fundamental case in Fluid Mechanics due to the wide spectra of instability modes/flow patterns that can be obtained in the gap. These flow instabilities are caused by the excessive increase of the inertial forces against the viscous forces, as the Reynolds number - defined as $Re = \rho \Omega R \delta / \eta$, where ρ is the density, *R* the radius of the inner cylinder, Ω

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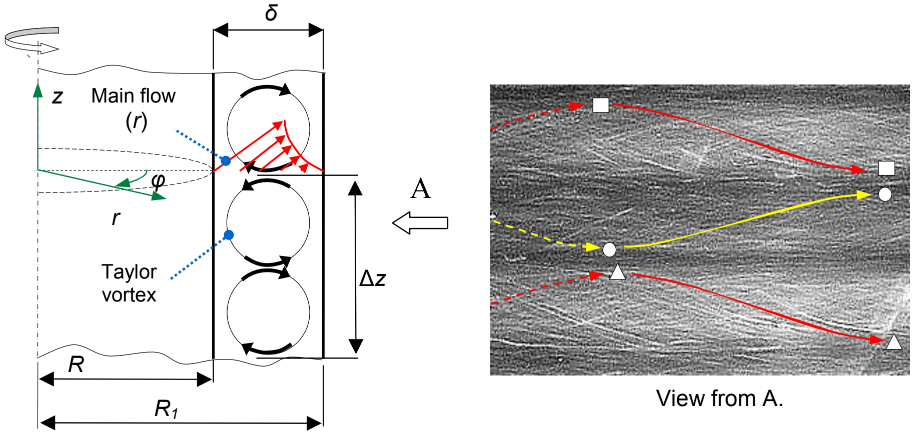

View from A.

Fig. 1. The structure of Taylor vortices, schematic drawing (left; after [2]) and experimental visualization (right) illustrating the 3D character of the flow, obtained by superimposing the toroidal vortices on the main flow.

the angular velocity of the inner cylinder, δ the gap width and η the dynamic viscosity - is increased. This leads to the transition from a one-dimensional flow – the laminar Couette flow – to various three dimensional flow patterns, as function of the imposed disturbances and their magnitude. . In the case of disturbances generated by the increase in *Re*, and for a simple configuration in which the inner cylinder is stationary and the outer one is at rest, the first instability mode is composed of vertically counter-rotating toroidal vortices named Taylor vortices in the honor of the pioneering work [1] of Sir G. I. Taylor (Fig. 1). By further increase of *Re* wavy vortices are developing - complex structures that involve significant fluid exchange between neighboring vortices, see [3] - and turbulent Taylor vortices, axisymmetric Taylor-like vortices of higher intensity, see [4].

In recent years there has been special attention regarding the possible use of the transitional flows in TC for applications such as mixing and chemical reactors, see for example [5], [6] and [7]. Following this line, the present work is a cooperation between the REOROM Group of Politehnica University of Bucharest, Romania and Institut für Thermische Verfahrenstechnik, Karlsruher Institut für Technologie (KIT), Germany. Previous studies of the two groups involved the characterization of mixing efficiency experimentally (Particle image Velocimetry and Planar Laser induced Flourescence) and numerically (see [7] and Fig. 2). Using a Poiseuille flow superimposed on the base flow, to enhance fluid transport along the fluid column and limit the backflow, Racina and Kind (2008) found a uniform distribution of mixing intensity in the flow field with the mesomixing level (mixing inside a vortex) as limiting for the whole process [7], [8]. Numerically, Kádár and Bălan (2009) analyzed the simple TC flow and found as a requirement for proper mixing the use of flow patterns superior to the Taylor

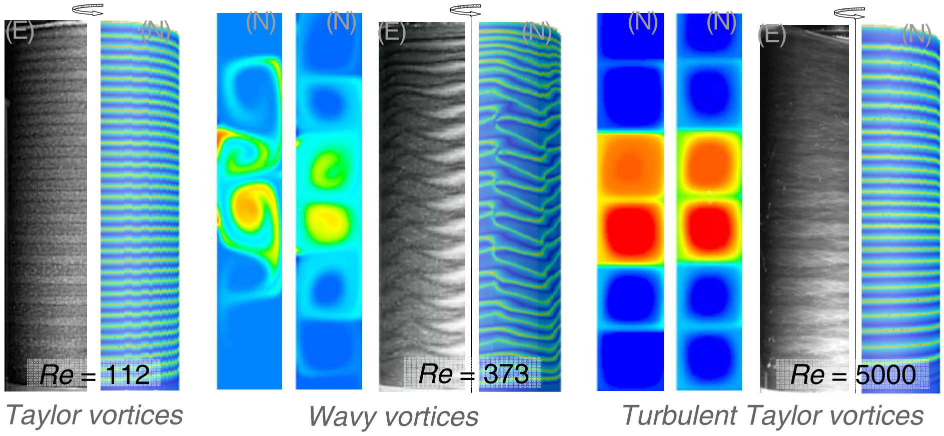

Fig. 2. Flow patterns (experimental, E, and numerical, N) and scalar mixing (numerical) in Taylor-Couette flow.

vortices, and namely the wavy and turbulent Taylor vortices, the first instability mode (Taylor vortices) being more suitable for separation processes, see [9]. Again, mixing at mesoscale limited the mixing performance of the turbulent vortices. In parallel, Kádár and Bălan (2008) investigated the influence of elasticity on flow behavior, and found no significant change in the flow behavior for weakly elastic polymer solutions. However, for increasing elasticity, they showed how the patterns can be altered, for example by extending the axial wavelength of the Taylor vortices and suppression of wavy regime [10].

The second stage of the project is dedicated to the study of the polymerization process in TCR. In this paper premixed monomer-solvent solutions are polymerized to estimate the evolution of the material properties during polymerization and the hydrodynamic activation due to the flow. The study is important due to the development of the rheological properties during reaction that in turn can affect the flow behavior and therefore the flow and therefore the mixing characteristics.

2. Experimental setup and procedure

The TCR built at KIT is presented in Fig. 3. The installation has a coooling/heating system as well as other features which are not discussed here. The characteristic parameters of the TC installation are radius ratio $R/R_1 = 0.889$ and aspect ratio $L/\delta = 68.4$. The free radical polymerization of Methylmethacrylate (MMA) was chosen as an example reaction. The monomer was premixed outside the reactor with a solvent, in this case Xylene (X), in order to avoid the solidification of the product at the end of reaction and the so-called gel effect (Trommsdorff-Norrish effect). In addition, the presence of the solvent

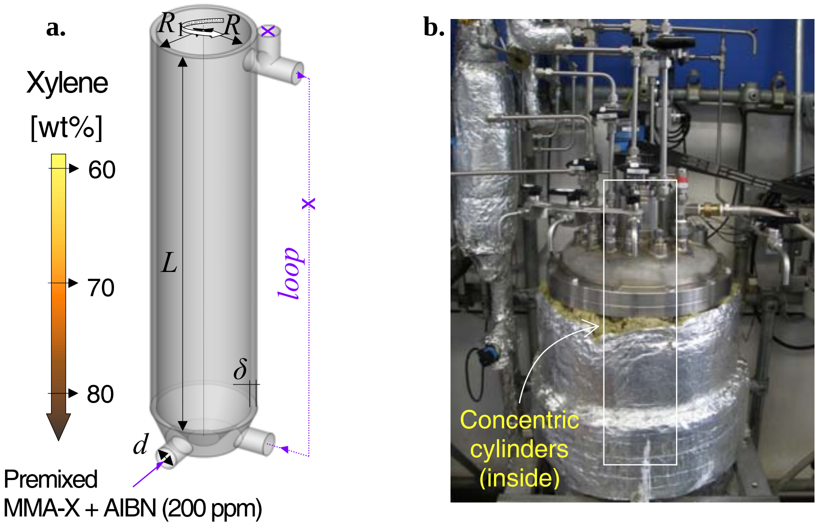

Fig. 3. The Taylor-Couette reactor used in the experiments (a) schematic representation of the concentric cylinders and (b) picture of the entire system.

has other positive effects, such as limiting the viscosity and elasticity increase during reaction, effects which are quantified in this paper. The reaction takes place at a temperature of 80°C and is triggered with the aid of an initiator, Azobisisobutyronitrile (200 ppm). The independent variables in the experiments are: solvent concentration (60, 70 and 80 wt% Xylene), reaction time and angular velocity of the inner cylinder ($\Omega = 0$, 7.4, 40, 52 and 66 rad/s). During the reaction small samples are extracted from the reactor and are quickly mixed with a reaction inhibitor and then stored at -30°C in order to stop the reaction. Subsequently, the samples were tested on a Paar Physica MCR101 rheometer, for rheological parameters, on a Gel Permeation Chromatograph (GPC) for molecular weight measurements and subjected to controlled drying to determine the conversion (the percentage of monomer that is transformed into oligomer/polymer).

3. Experimental results

The rheological properties were performed using steady shear and oscillatory shear measurements. The later ones were preferred whenever possible, meaning as long as the viscosity was high enough. During the tests, three types of rheological behaviors were observed. These are illustrated in Fig. 4.a in a reaction time - solvent concentration - angular velocity space. The first, in which the shear thinning of the fluid was neglectable and the elastic modulus unmeasurable,

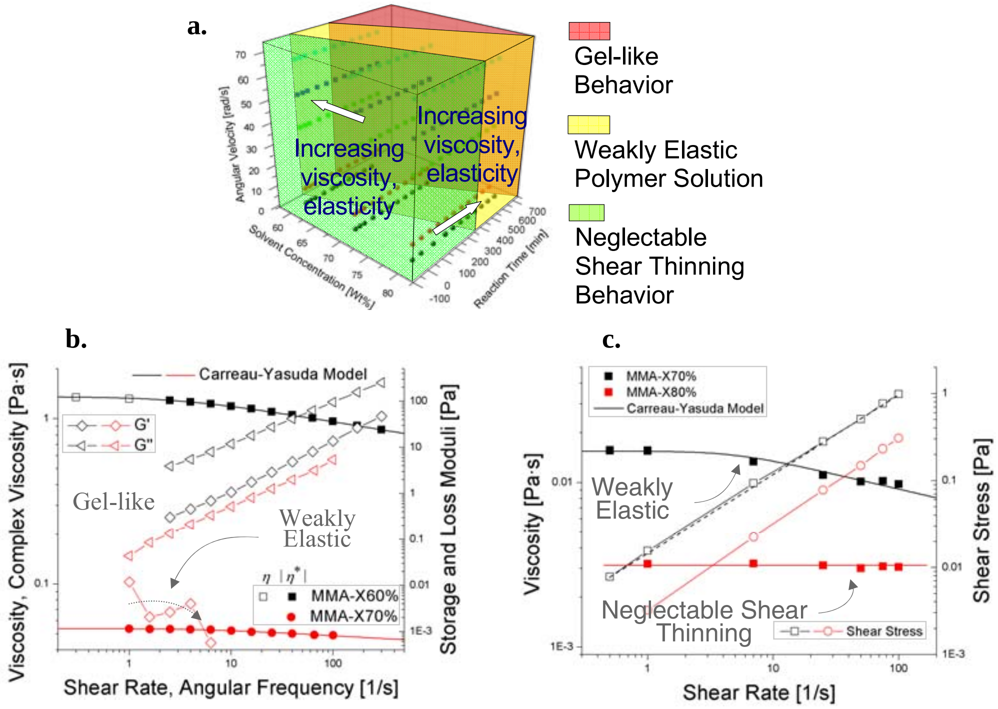

Fig. 4. The rheological behavior observed during tests: (a) general representation in the reaction time - solvent concentration - angular velocity space, (b) weakly elastic and gel-like behavior in oscillatory and steady shear tests and (c) weakly elastic and neglectable shear thinning behavior in steady shear tests.

occurred for low concentrations of solvent and at the beginning of the reaction for all solvent concentrations (see Fig. 4.c). For the second type of behavior, the shear thinning character of viscosity is significant but the elastic modulus would fall with increasing angular frequency, behavior named here as weakly elastic. The third type of behavior is characterized by almost parallel storage and loss moduli, as function of angular frequency, which is here named gel-like behavior [11]. This behavior characterizes low concentrations of solvent and occurs towards the end of the reaction (for Xylene 80wt% this phenomena was absent).

Concerning the temporal evolution of measured material properties, the results are presented in Fig. 5, for tests with Xylene concentration of 60wt% (the results are representative for the other solvent concentrations as well). At this point we are interested in the hydrodynamic activation of the reaction, defined as the influence of the angular velocity of the inner cylinder on the measured parameters. Thus, one can see that at the beginning of the reaction, conversion increases with increasing Ω whilst towards the end there is no significant

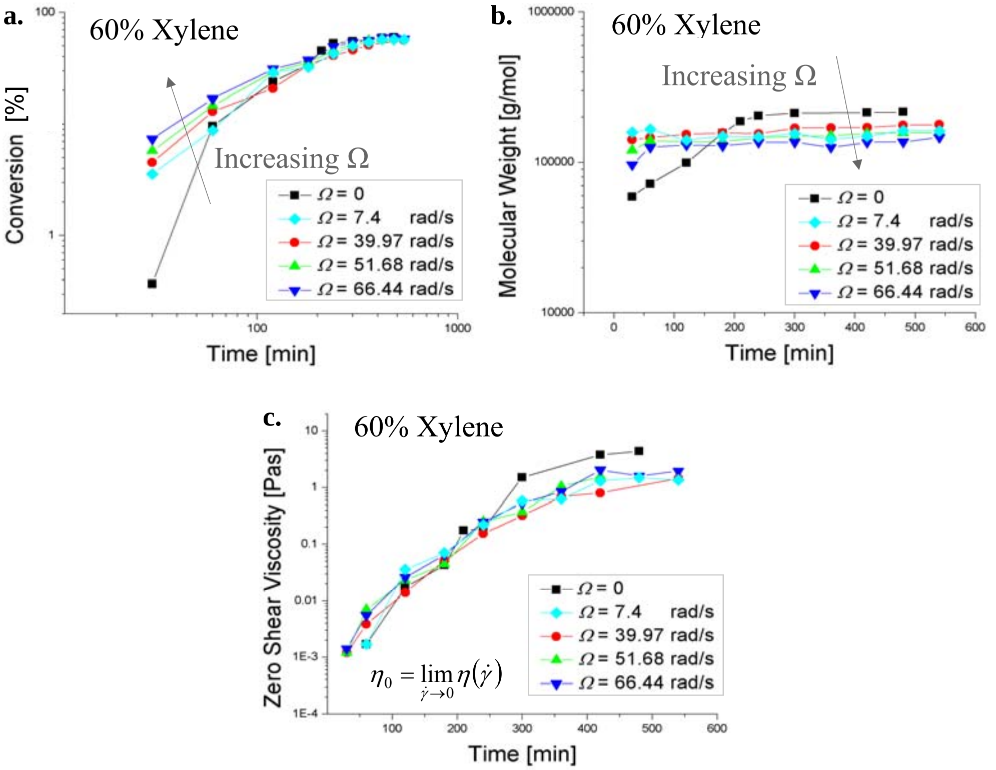

Fig. 5. Temporal evolution of measured parameters: (a) conversion, (b) molecular weight, and (c) zero shear viscosity.

difference between tests (Fig. 5.a). For Molecular weight (Fig. 5.b) there is a significant qualitative difference between tests with $\Omega = 0$ (no hydrodynamic activation) and the ones with $\Omega \neq 0$. Towards the end of the reaction though, the molecular weight decreases with increasing Ω. In the case of the Zero shear viscosity defined as the viscosity at vanishing shear rates, the differences, the influence of the hydrodynamic activation is not significant, although the $\Omega = 0$ tests is crossing the other curves in a similar manner as the molecular weight.

Given the angular velocity is constant during reaction, the Reynolds number is a function of the viscosity which is a function of reaction time, $Re = f\left[\eta|_{\dot\gamma}(t)\right]$. Thus, using the data such as that presented in Fig. 4, one can compute *Re*, result which is of crucial importance in evaluating the flow characteristics, and thus the interpretation of overall results and estimation of the outcome of future tests that would involve mixing. The results, for all Xylene concentrations are presented in Fig. 6. The critical parameter, Re_{cr1} in the figure are a result of experiments and linear stability theory for the flow of Newtonian

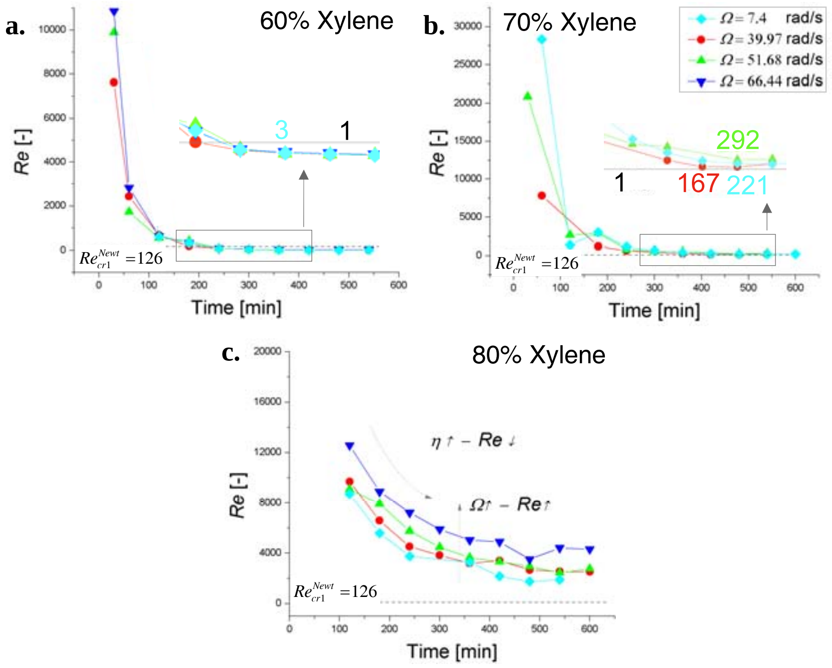

Fig. 6. Flow behavior during reaction represented as the Reynolds number as function of time, for (a) 60% Xylene, (b) 70% Xylene and (c) 80%Xylene.

fluids (for such large aspect ratios and radios ratios, the Taylor vortices appear in a very narrow range of *Re*, followed by the wavy regime). Thus one can see that for 70wt% and 80wt% Xylene tests, *Re* is well in the unstable zone. However, one must also note that the influence of elasticity on the value of the critical parameters has not been yet considered, this part of the work being currently in progress.

4. Conclusions

In this work premixed monomer-solvent mixtures have been polymerized in a Taylor-Couette reactor. The results show a weak dependence of the measured parameters on the hydrodynamic activation, defined as their dependence on the angular velocity. The rheological boundaries where a Newtonian mixing model, with minor corrections, could be applied, was estimated (low elasticity, to preserve Newtonian flow patterns, and low viscosity to be in the desired mixing regime). The results presented in this paper constitute prerequisites for the study of relationship between mixing and a chemical reaction in a Taylor-Couette polymerization reactor.

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