Polymer Engineering

Reactive Polymerization

KEYWORDS: Reaction Injection Moulding, Reactive Extruder, Formulation Device; Product Development

Implementing new formulations for reactive polymerisations in industry requires the definition of guidelines to avoid process design flaws. This research introduces a rotational device as a formulation lab methodology that mimics the evolution of mixing scales in industrial processes. A general design equation is proposed for Reaction Injection Moulding mixing heads, which eliminates operation flaws due to mixing issues. Fundamental studies on mixing mechanisms were extended to reactive extrusion for bio-polyurethanes (bio-PUs).

Introduction

LSRE-LCM has a long track record of research on Reaction Injecting Mould (RIM), a topic that has been running internally since the 1990s. LSRE-LCM is recognised in the industry as a leading group in this research field. Three main contributions in this field were the development of the technology RIMcop, with a filed patent in 2005; the development of a design equation that enabled mixing heads based on Confined Impinging Jets (CIJs) mixers to operate without flow restrictors; and the start-up of the spin-off company MICE-molds in 2013 based on the RIM new technologies introduced at LSRE-LCM. MICE-molds is still in the market and keeps a growing activity based on LSRE-LCM technologies, and its CEO did his PhD dissertation in this group.

In the current period, the main research topic was product development for RIM and adapting the process to product formulation. Implementing new formulations/products in RIM processes is a complex task since the operational conditions must be adjusted considering the stoichiometry ratios of monomers and the operational conditions promoting efficient mixing between them. Currently, reactive polymerisation formulations are developed in pilot RIM machines with industrial dimensions, typicaly above 10 kg/min. So, several kilograms of raw materials are used for each formulation and processing condition. Mixing conditions at industrial units are not easily mimicked at lab-scale formulation tests because the lab devices are not capable of setting the same short mixing times as industrial machines. This work proposes a rotational lab-scale fomulator that mimics the indutrial mixing conditions.

In industrial RIM machines, CIJs are widely used as mixing heads, but the control of mixing has always been the Achilles' heel of this technology. For mixing of two liquid streams, the inlet Reynolds number must be above the critical value, $\mathrm{Re_c} > 150$ for the more viscous fluid and the impingement point position of the monomers jets in the CIJs must be at the centre of the chamber with a tolerance of less than 10%. A design equation that accurately predicts the impingement point position for a set of operational and design parameters was developed, which con.

The LSRE-LCM research team has also been focused on reactive extrusion processes for the production of bio-PUs. This work aims to develop a process to produce bioPUs for incorporation into footwear, one of the most important industries in Portugal.

Current Development

In RIM, the efficient mixing of the two liquid monomers being impinged in the CIJs only occurs due to the onset of the self-sustainable chaotic flow regime. This flow regime is characterised by the formation of a vortex street downstream of the injector axis. These dynamic structures play an essential role in stretching the interfacial area between the monomers, promoting striation thinning. A rotational device is proposed for fast lab-scale formulation development, which enables mimicking the stretching and folding in industrial RIM machines mixing heads. The geometrical configurations of the rotational device are the same as those of rheometric devices.

Mixing in rotational devices was studied from 3D CFD simulations. The rotational device consists of two parallel plates, a rotating top plate and a stationary bottom plate, i.e. the exact configuration of plate-plate rheometer. The mixing of working fluids was simulated with the Volume-Of-Fluid model. The two fluids are initially side by side (Topology 1) or in two horizontal layers (Topology 2). Fig.1 shows that, for Topology 1, the rotation of the top plate promotes the stretching of the interface between phases and the formation of a lamellar structure by the overlapping of phases.

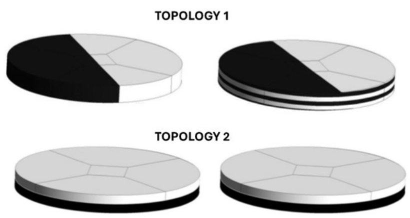

Fig 1. Contour maps of phases in rotational device for different topologies (Topology 1 – fluids are side by side; Topology 2 – fluids are over each other) at initial time and after 3 turns of the top plate.

A method that tracks an infinitesimal element stretched in a shear flow was implemented to calculate the striation thickness decay. For that, an incompressible fluid was considered, and the striation thickness is given by $\frac{s(t)}{s_o} = 1/\sqrt{1+\left(\frac{\omega R_P t}{h_P}\right)^2}$, where s_o is the initial striation thickness at $t = 0$, h_P is the gap between the two parallel plates, ω is the angular velocity of the top plate and R_P is the radius of the top plate. The validation of this expression from CFD simulations enables the design of the operation conditions, such as the velocity of the top plate and the number of rotations, to achieve the desired striation thickness in the formulation process.

The screening of 2D mixing information generated in the RIM machines mixing chamber (CIJ mixer) is successfully made from the spatial identification of striation thickness decay. Fig. 2 shows the analytical expressions of the angular speed at the top plate that promote mimicking the same mixing conditions generated in each region of a CIJ mixing chamber (pancake shearing, engulfing vortices and CIJ runner).

The topology of mixing, i.e., the initial position of a reactant in relation to the other, was also explored in this work using well-defined flows such as those occurring in rheometric devices. For Topology 1, the induced shear stretches out the interface between fluids, creating striation thinning lamellae (Fig.1). For Topology 2, the mixing scales and the interface of both phases are kept unchanged (Fig.1).

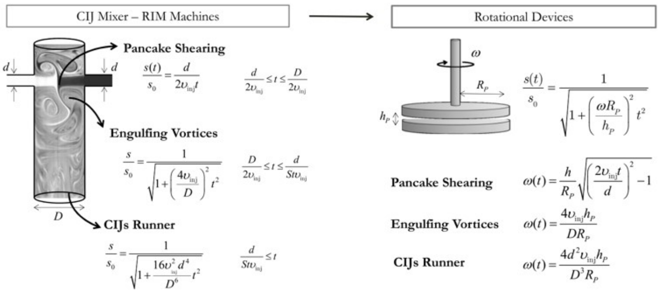

Fig 2. Mixing length scales evolution in CIJ mixers and related evolution in a plate-plate rheometer.

Different topologies of the fluid interface are associated with different flow regimes. An analogy between the topology set in the plate-plate geometry and CIJ mixers flow regimes can be made: when the two fluids are initially placed side-by-side in the rotational devices, this corresponds to chaotic flow regimes, where there is the formation of vortices that reduce the scales of the lamella of fluids; when the fluids are initially placed one on top of the other, it corresponds to the segregated flow regime where the interface between two phases is preserved without any change.

A model that accurately describes the Impingement Point (IP) position in the CIJs enables the design of operational conditions and the mixer geometry. Three balance models were considered for the description of the IP position in the mixing chamber: elastic analogue model (EAM), kinetic energy model (KEM) and momentum model (MM). These models consider the physical properties of fluids, the conditions at the inlets and CIJ geometrical parameters. EAM, based on the analogy of two jets and two springs, gives a good prediction of the IP position for similar fluids. KEM and MM were proposed for the first time and are based on the balance of kinetic energy and momentum of jets at the IP position, respectively. Experimental and numerical results were used to validate EAM, KEM and MM. Fig.3 shows the dimensionless IP position, ξ , determined from experimental and numerical results for two different conditions: a viscosity ratio of 5 and a density ratio of 1; and a viscosity ratio of 5 and a density ratio of 10. Fig.3 shows that KEM is the General Design Equation (GDE) equation for RIM processes because it has a broader validity range. This research was a collaboration with Professor Cláudio Fonte from the University of Manchester.

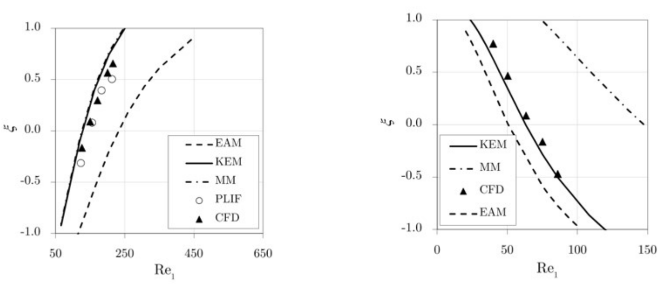

Fig 3. Dimensionless IP point determined from EAM, KEM, MM, CFD results and PLIF data for the mixing of dissimilar fluids with a viscosity ratio 5 and density ratio of 1 and Re_2=45 (left figure) and density ratio of 10 and Re_2=45 (right figure).

Reactive extrusion is a process recently studied at LSRE-LCM to develop a formulation methodology for bio-PUs for footwear applications. This is one of Portugal's most important industrial sectors, particularly in the North region. An experimental protocol to assess the reactive polymers formulations has been developed from CFD simulations and linked to the conditions in an industrial reactive extruder. The objective is tailoring a lab-scale screw extruder that enables the formulation of polymers with small quantities of material. Fig 4. shows the CFD simulation of a single screw rotating at 10 RPM. The project's partners are a footwear company, Atlanta, Instituto Politécnico de Bragança and Centro Tecnológico do Calçado. This project is running under the goals of the Resilience and Recuperation Plan for the Portuguese industry and addresses one of the primary objectives of the footwear

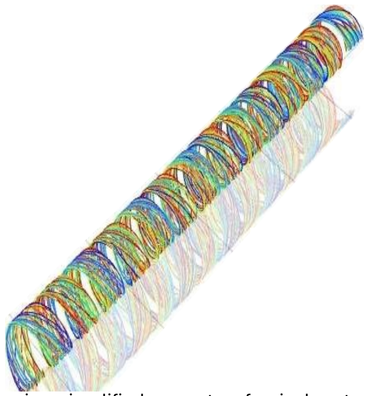

Fig 4. Streamlines in a simplified geometry of a single extruder for a rotation of 10 rpm.

sector in Portugal, the incorporation of biobased polymers.

Future Perspectives

In the future, a significant goal is the development of new formulations and processes that can be designed using rotational rheometric devices.

An analytical equation is proposed to describe the impingement point position in a CIJ mixing chamber. The validation addressed in this work has a massive contribution to the design of industrial processes in CIJ mixers. This will be further exploited in industry, with a focus on industrial RIM processes for BioPUs. A project was already submitted in this field and got the EUREKA approval stamp.

Screw extruders will be further studied during the BioShoes4All project. The main purpose of this project is to introduce a protocol that bridges the process conditions for bio-PUs at the lab scale using small quantities of raw materials for industrial extrusion processes. Elham Delvar, a PhD student, will continue these studies in her PhD work, supported by the FCT scholarship 2023.01245.BD.

Related Sustainable Development Goals

Outputs

PhD Theses

[1] Margarida Brito, *Mixing Mechanisms in 2D Reactors,* PDEQB, FEUP, 2021

Selected Publications

[1] Brito MSCA et al., Chemical Engineering Journal, 465, 142892, (2023);
[2] Brito, M.S.C.A., et al. AIChE Journal, 68, 17597 (2022).

Team

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Funding

BioShoes4All, PRR-000011, 2021-2025,
2Dmix, POCI-01-0145-FEDER-016851, 2016-2019
LSRE-LCM Base Funding, UIDB/50020/2020, 2020-2023
LSRE-LCM Programmatic Funding, UIDP/50020/2020, 2020-2023
LA LSRE-LCM Funding, UID/EQU/50020/2019, 2019
LA LSRE-LCM Funding, POCI-01-0145-FEDER-006984,2013-2018
FCT Scholarships: PD/BD/135060/2017 (M. Brito)