Recent Advances in Combining the Fields of Polymer Continuous Flow and Microwave-Assisted Chemistry

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In a typical batch reaction, starting materials are added to the reaction vessel at the beginning of the reaction, product is formed in the same vessel, and the product is then isolated, purified, or processed.[1] Alternatively, chemistry can be performed in a continuous flow system, where starting material is continually fed into a tubular reactor (**Fig. 1)**. As the starting material flows through the reactor, the chemical reaction will occur to generate a continuous stream of product, where the reaction time is equal to the residence time within the reactor. Mathematically, residence time is defined as the volume of the reactor divided by the flow rate.[2] Tubular reactors generally have diameters on the millimeter scale, meaning only a small volume of the starting material is fed into the reactor at a time.[3] Thus, continuous flow systems are a safer method of handling hazardous chemicals. Additionally, because the surface area of the tube is large relative to the volume of the reacting solution, the increased heat dissipation of the system can be utilized to perform highly exothermic reactions that would be unsafe in a batch process.[3,4]

Figure 1. Simple schematic of a tubular flow reactor for continuous flow.[2]

The speed at which fluids are injected into a flow reactor will influence how the fluid flows within the tube (**Fig. 2**). For a solution that is slowly injected, the flow is laminar and has a parabolic velocity profile, in which the fluid in the center of the tube travels at a faster rate than the fluid near the walls. The lower velocity near the walls is due to frictional forces between the tube and fluid. The nonuniformity of this profile means that, for material initially injected at the same time, there will be some difference in the residence time, leading to a broad residence time distribution (RTD). This distribution, in turn, can lead to undesirable side reactions because some of the fluid stays in the reactor for long times. In contrast, when fluid is injected into a flow reactor at high speeds, a plug flow will be attained, in which the velocity profile of the fluid is the same along the entire diameter of the tube. In this case, material that is injected at the same time will also be eluted at the same time, producing a narrow residence time distribution and a more uniform product distribution. In addition to flow speed, other factors that influence the flow are the viscosity and density of the fluid.[4]

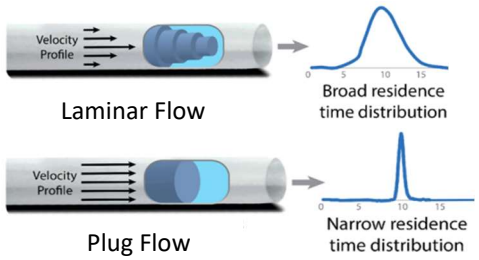

Figure 2. Laminar flow, plug flow, and the associated RTD.[4]

Another advancing field is the use of microwaves (MW) to promote chemical reactions or processes, as an alternative to conventional heating methods. Whereas conventional heating relies on heat transfer, MW heating proceeds via interaction of the material with an electromagnetic field, such that the MW energy is converted to thermal energy within the material. This mechanism allows for rapid, selective, and non-contact heating of materials, enabling reactions to proceed at a faster rate and with greater selectivity and yield. Further, this high efficiency of energy utilization

makes it a less costly heat source.[5] The ability of a material to be heated by MW irradiation depends on two main factors: loss tangent (tan δ) and penetration depth (D_p). The loss tangent of a material describes its ability to absorb MW energy: it is proportional to the conversion efficiency of electromagnetic radiation to heat (dielectric loss, ε″) and inversely proportional to the polarizability of the material by the field (dielectric constant, ε′). This value is particularly important for the solvent used in the reaction. The greater the loss tangent of a material, the greater its ability to be heated by MW. Penetration depth describes the depth in the material at which the electric power is half of that at the surface: it is also related to the dielectric properties of the material.[6,7]

The limitation of MW heating is that, at typical operating frequencies, D_p is only a few centimeters. Thus, for most reaction vessels, only the outer surface of the solution will be heated by MW, while the central material is heated by convection. This non-uniformity decreases the efficiency of MW heating and negates many of its advantages. The combination of MW heating with continuous flow, however, offers a strategy to overcome the limitation of D_p. Because continuous flow reactor tubing has a diameter typically on the millimeter scale, even materials with low D_p can be uniformly heated by MW irradiation. This is not the case for conventional heating of fluid in a tubular reactor, where there is still a temperature gradient even at small diameters (**Fig. 3**). The combination of flow and MW heating creates a process that is fast, selective, reproducible, scalable, and energy efficient.[6]

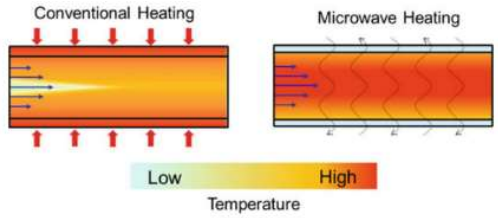

Figure 3. Temperature distribution of conventional and microwave heating in flow.[7]

Although microwave-assisted chemistry has been performed since 1986[6] and continuous flow processes have been implemented in polymer chemistry for multiple decades,[4] in recent years the combination of these two techniques has been increasingly investigated. Here we will give examples from polymer chemistry.

In 2022, Saleem et al. used microwave-promoted continuous flow to synthesize metal/polymeric nanocomposites (**Fig. 4**).[8] By feeding the polymer matrix, polyurethane, and the silver precursor ($AgNO_3$) into a microwave reactor, and varying parameters such as microwave power, concentration, and flow rate, they were able to synthesize uniform, spherical nanocomposites with small diameters (< 10 nm) at 40 °C. In doing this, they related microwave power to the nucleation rate of the silver nanoparticles, and flow rate to the residence/irradiation time of the particles within the microwave reactor. Their MW-heated flow reactor far outperformed a similar conventionally-heated flow apparatus, which failed to produce any nanocomposites, and also outperformed a MW-assisted batch reactor, which produced large (>100 nm) nanoparticles but only at temperatures near 70 °C. The resulting biocompatible nanocomposites were

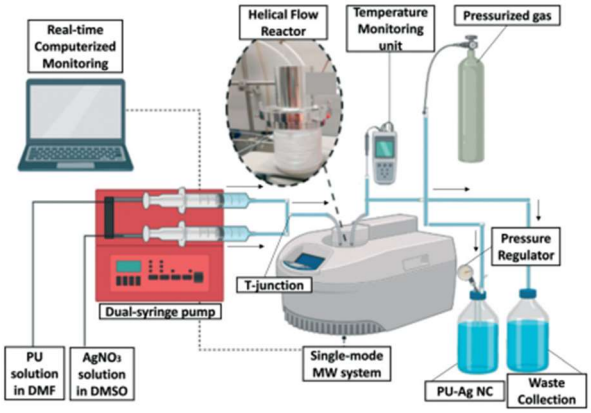

Figure 4. MW flow reactor setup for PU/Ag nanocomposite synthesis.[8]

then incubated with three different bacteria to show their effectiveness as antimicrobials against several disease-causing organisms.[8]

Another recent publication examined the use of microwave heating in a continuous flow process to 3D print a polyamide thermoplastic reinforced with carbon fibers (**Fig. 5**).[9] Carbon fiber, synthesized from polyacrylonitrile (PAN) via a series of heating and processing steps, is a high-tech, carbon-rich material.[10] When carbon fibers are embedded into a polymeric matrix, the resulting carbon-fiber reinforced plastics (CFRP) have enhanced material properties and strength while being incredibly light, making them useful in applications such as aerospace, automotive, and medical technology. Producing CFRPs by 3D printing enables embedding of continuous carbon-fibers (as opposed to short segments of carbon fibers) into the polymer matrix. With microwaves, the heating of the filament is instantaneous, selective, low-energy, and contact-free, allowing for fast printing relative to conventional heating methods. In this paper, the authors precisely tuned the filament temperature as a function of MW power in order to print carbon-fiber reinforced polyamide at fast speeds (50 mm/s) without any loss in tensile strength.[9]

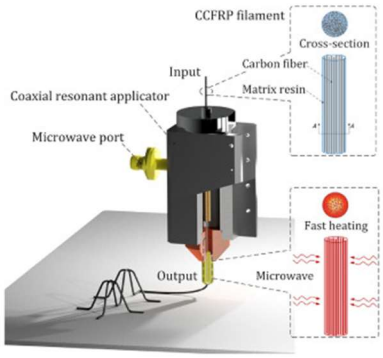

Figure 5. 3D printing set up of CFRP.[9]

Microwave and continuous flow can also be beneficial in performing chemical reactions. The polymerization of poly(2-oxazolines) (POxs), a versatile polymer with applications related to their biocompatibility and thermoreversibility, is performed via the cationic ring opening polymerization (ROP) of 2-oxazoline monomers.[11] However, the problem with this reaction is that the weakly nucleophilic 2-oxazoline must act as a nucleophile during propagation, so the reaction proceeds very slowly, even at elevated temperatures. To overcome this limitation, Petit et al. hypothesized that the use of microwave heating and continuous flow could accelerate the polymerization, control the occurrence of side reactions, decrease the hazards associated with performing the reaction at high temperatures, and improve the efficiency of energy, time, space, and material use. In their flow reactor, one syringe injected monomer and initiator dissolved in an ionic liquid and a second syringe injected oil, such that reactive, MW-absorbing droplets were formed within the inert, non-MW-absorbing oil phase (**Fig. 6**). By controlling the power of the microwave source, temperatures of 80-140 °C were achieved, resulting in an increase in the rate of the polymerization.[11]

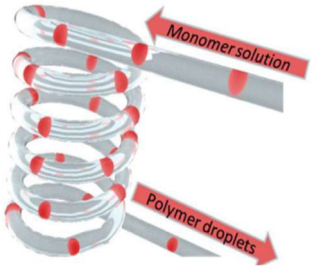

Figure 6. Droplet flow schematic for 2-oxazoline ROP.[11]

The combination of continuous flow and microwave-assisted chemistry has led to new advancements in polymer chemistry, and has led to increases in energy-efficiency, reaction rates, selectivity, safety, and reproducibility. As these technologies continue to be combined for different applications, their synergistic advancements have the potential for even greater impact.

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