

Microwave-assisted chemical recycling for polymeric waste valorisation

I. Julián, C. González-Niño, A. Frisa-Rubio, N. García-Polanco

CIRCE Foundation, Zaragoza, Spain

iajulian@fcirce.es

Abstract — Microwave-assisted chemical recycling is envisioned as a promising strategy to recycle and valorise plastic residues in a cost-effective and energy-efficient way. The selective microwave heating provides a three-fold process intensification with respect to conventional heating technologies that rely on fossil fuels: a) electrification and, thus, possibility to use renewable energies to run the system, b) severe reduction of sample heating and cooling times, c) remarkable decrease of operational temperatures for a certain polymer valorisation degree. The chemical recycling requires, however, a very accurate temperature control to conduct the plastic depolymerization process properly and avoid undesired side reactions. In this frame, the purpose of the current work is to model and simulate the heating pattern of a one-liter polymer solution, i.e. polyamide 66, in a multimode MW-assisted reactor prototype and to validate the model with experimental temperature measurements, as a previous step for technology scaling.

Keywords — electromagnetic modeling, dielectric heating, recycling, plastics industry.

I. INTRODUCTION

The increasing production of plastic waste and the public awareness of plastic pollution have motivated an intense research activity devoted to plastics recycling [1]. Handling plastic waste through recycling allows extending the life of polymeric materials, avoiding recurrence to incineration or landfilling [2]. Chemical recycling has been envisioned as an alternative to the well established mechanical recycling since it allows for the production of value-added chemicals, fuels and monomers recovery [3]. Specifically, chemical recycling enables the obtention of virgin monomers by depolymerisation to create new polymers, ideally having the same mechanical and thermal properties as the originals [4]. In order to achieve this, the temperature control along the depolymerization process is critical. Should deviations occur, the degree of depolymerization becomes uncertain and the formation of undesired side products may occur. Apart from this, the main challenge of the chemical-based recycling technologies is to make this depolymerization process economically viable [5].

Microwave-assisted chemical recycling emerged as a promising strategy to recycle and valorise plastic residues in a cost-effective and energy-efficient way [6]. Among the advantages of this system, the electrification of the recycling process would allow the reactor to be fueled with renewable-based energy. In addition, the selective heating provided by microwave irradiation may drastically reduce processing times and operational temperature [7, 8] to attain certain polymer

degradation degree. Furthermore, the contactless volumetric heating provides an intrinsic energy efficiency against conventionally heated systems, in which a portion of the input power is lost in the surrounding atmosphere heating.

The main limitation of multimode microwave cavities is the eventual formation of hot spots that lead to an uneven temperature distribution along the sample, specially when processing relevant sample sizes [9].

In this frame, the development of large scale microwave-assisted chemical recycling technologies requires an intense research activity in the design, modeling and testing of applicators that are able to provide a homogeneous temperature distribution within big polymer solution samples [7].

This MW-assisted technology has been already validated for polyamide and polyurethane depolymerization purposes at bench scale (vessel capacity: 10 mL) [6]. In particular, it was shown that the depolymerization of polyamide 66 (PA-66) into adipic acid and hexamethylene diamine monomers under microwave assisted acidolysis was conducted with a nearly 100% yield to the monomers at operation temperatures as low as 180°C and residence times as low as 10 minutes [6].

In order to fill the gap between bench scale tests and desired industrial process capacities (100 L – 1 m³), this work addresses the modelling, simulation and experimental validation of the heating pattern of a new microwave reactor prototype able to process up to 1 L polymer waste samples. This represents a two orders of magnitude greater system than that recently reported in literature for the proof-of-concept of the technology [6].

In this work, the depolymerization of polyamide 66 (PA-66) into adipic acid and hexamethylene diamine monomers under microwave assisted acidolysis has been selected as the target process. The composition of the acidic solution was selected based on the optimized values obtained by [6] in their bench scale depolymerization tests, i.e. 14 wt% HCl, HCl/amide = 1.25 mol/mol.

Experimental sample heating and temperature monitoring tests were conducted in the mentioned MW-oven prototype (Figure 1.a) whereas MW-heating simulations were performed for a mimicked cavity domain (Figure 1.c) using the COMSOL Multiphysics software, coupling electromagnetic and heat transfer physics.

A major challenge in the simulation model is to account for the mode stirrers (Figure 1.b) rotation at the waveguide-end of the four input ports that the prototype has, upon sample heating [10, 11].

The novelty of the proposed model lies in the transient integration of mode stirrers rotation and, thus, electromagnetic (EM) field distribution change, with sample heating. Assuming that the rotation speed of the mode stirrers is much faster than the transient sample heating, the EM fields at different positions of the mode stirrers can be computed and averaged out for a given time step. The averaged EM field distribution at each time step can be then employed as input value for resolving heat transfer equations in the subsequent time step. As a result, the implementation of a moving mesh is avoided and the computational cost is drastically reduced, while preserving a consistent and reliable solution for the simulated system.

II. EXPERIMENTAL SET-UP

The experimental set-up consists in a microwave oven (MRA Instruments – BP-211(/50)) having four input ports with mode stirrers and powered by a magnetron that delivers an input power of 3 kW working at 2.45 GHz. The oven is equipped with three temperature probes: K-type thermocouple, pyrometer and a thermal camera. In addition, it holds a rotor and stirrer for sample temperature homogeneizing. The load (i.e. polymer solution) is placed in a 1 L quartz vessel within a closed PEEK chamber. The chamber can be pressurized up to 20 bar. Both quartz and PEEK materials were selected due to their transparency to microwave radiation. The dimensions of the upper chokes were selected to avoid MW leaking. The temperature control loop (either via thermocouple or pyrometer) provided with the oven allows inducing heating ramps and setting steady temperature operation. The microwave oven is depicted in Figure 1.a.

The temperature distribution maps were obtained with a FLIR E6-XT infrared camera. The measurement protocol was as follows: 1) the cold polymer solution was poured into the quartz vessel and heated up to a prescribed temperature (Figure 2.a); 2) the MW generator was switched off and the oven door was opened; 3) the infrared recorded the map of quartz vessel temperature in contact with the polymer solution (Figure 2.b).

The emissivity calibration enabled the estimation of the real temperature of the polymer solution directly from the quartz vessel temperature measurements.

Heating tests were performed with (Figure 2.c) and without (Figure 2.b) stirring the solution. An in-house developed Matlab code was created to quantify the radial and axial temperature gradients based on the acquired thermal images (Figure 2.d).

III. NUMERICAL MODEL

A. Model Set-up

A rectangular multimodal cavity with four input ports and mode stirrers working at a frequency of 2.45 GHz has been modelled (Figure 1a). The four mode stirrers enable homogenising the EM field distribution within the heated sample in the absence of a rotary plate. The MW oven inner dimensions are: 53.5 (height) x 23.5 (width) x 33 (depth) cm. The load dimensions are: 8.4 (diameter) x 17.75 (height) cm, being its bottom end placed at the centre of the cavity. The real

dielectric properties of the acidic polymeric solution at room temperature (T_{amb}) were included in the model, i.e. dielectric constant (ϵ') and loss factor (ϵ''), being their values 5.34 and 0.29103 respectively. To account for the variation of the dielectric properties of the sample with temperature, the existing of $\epsilon'(T)$ and $\epsilon''(T)$ correlations for water at 2.45 GHz [12] were adopted, using the real room temperature values as correction factors, e.g. $\epsilon'(T)_{\text{sol}} = \epsilon'(T)_{\text{water}} \cdot \epsilon'(T_{\text{amb}})_{\text{sol}} / \epsilon'(T_{\text{amb}})_{\text{water}}$. This approach seems reasonable taking into account that water represents 83% of the solution volume, being the most MW absorbing material in the mixture. The power input of the simulated magnetron was set to 3 kW in order to mimic that of the available experimental set-up. The selected microwave susceptor is a cylindrically-shaped one-litter vessel containing an aqueous acidic polymer solution. The PEEK chamber and tank stirrer as well as the quartz vessel, muffle and Teflon structure were omitted in the COMSOL model for simplicity.

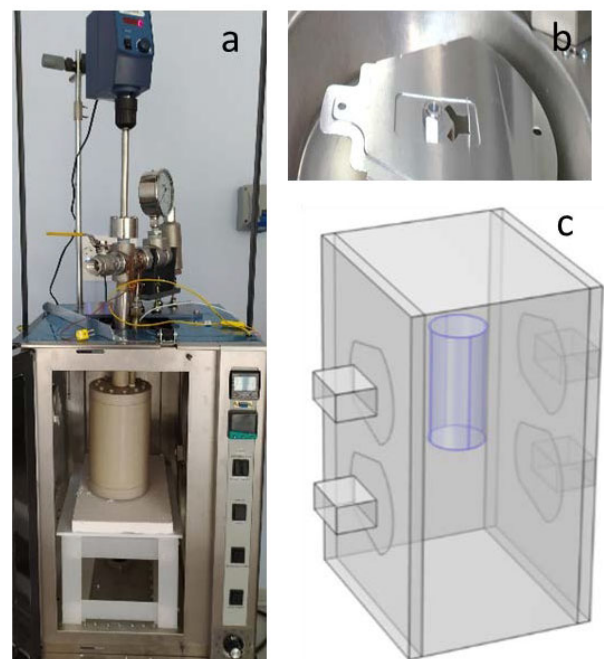


Fig. 1. a) experimental MW-assisted chemical recycling set-up, b) detail of the mode stirrer, c) simulation domain: rectangular cavity with four ports having mode stirrer and cylindrical MW susceptor containing the acidic polymer solution

B. Governing Equations

The Maxwell equations and energy conservation law included in the Radio Frequency (RF) module were used to simulate the electromagnetic heating process. Assuming a time-harmonic EM field, Maxwell equations are formulated as shown in equation 1, where ω is the angular velocity, σ is the electrical conductivity and \vec{E} is the complex-valued electric field. The electromagnetic losses considered in the model (resistive and magnetic losses) were calculated according to equations 2 and 3, respectively. In such equations, \vec{J} represents the current density, \vec{B} is the magnetic flux density, and \vec{H} is the magnetic field intensity.

$$\nabla \times \left(\frac{1}{\mu} \nabla \times \vec{E} \right) - (\omega^2 \epsilon - i\omega\sigma) \vec{E} = \vec{0} \quad (1)$$

$$Q_{rh} = \frac{1}{2} \text{Re}(\vec{J} \vec{E}^*) \quad (2)$$

$$Q_{ml} = \frac{1}{2} \text{Re}(i\omega \vec{B} \vec{H}^*) \quad (3)$$

In addition, two heat transfer mechanisms were considered in the model, i.e. convection and diffusion. Due to the eventual fluid motion along heating, the contributions of the convective, viscous flow and pressure terms were also included. The transient form of the heat transfer equation employed for the determination of the temperature field in the load domain is presented in equation 4.

$$c_p \rho \frac{dT}{dt} + \rho c_p \vec{u} \cdot \nabla T = \alpha_p T \left(\frac{\partial p}{\partial t} + \vec{u} \cdot \nabla p \right) + \tau : S + \nabla \cdot (k \nabla T) + q \quad (4)$$

First, the electromagnetic waves (frequency domain) model was solved for a different number of mode stirrer positions (4, 8, 12 and 16) using a GMRES linear system solver (generalized minimum residual). The EM field solutions of each mode stirrer position at a given time step were averaged out to get an apparent average EM field. This resulting EM field was then employed as input value for resolving the heat transfer model at the current time step and calculate sample heating. The transient heat transfer model was solved using a PARDISO solver (parallel sparse direct solver).

Impedance boundary conditions were imposed upon all sides of the cavity and the waveguides. The wave ports are located at the entrance of the waveguides (Figure 1.a) and configured to propagate through them in the transverse electric mode (TE₁₀).

A mesh independency test was conducted in order to avoid mesh-derived effects on both EM field and sample temperature results. The final mesh size (nearly 74000 elements) accomplished the recommendations regarding the fact that the wavelength at the employed irradiation frequency needs to be discretised into, at least, five elements along the air domain for proper convergence. In addition, the lossy material was discretised into 1 cm length elements for a better resolution in the temperature field distribution.

Furthermore, the number of stirrer positions was also evaluated in order to find a minimum number of averaged out mode stirrer positions per time step to attain certain case-independent sample heating rate.

IV. RESULTS

A. Experimental Heating Tests

Regarding the heating tests with and without tank stirring (Figure 2.c and 2.b, respectively) it was found that a stirring velocity of 300 rpm was able to homogenize the sample temperature with an axial and/or radial temperature gradient lower than 2°C in less than 30 seconds (Figure 2.d). In addition, it was observed that in spite of using mode stirrers, hot spots are formed within the vessel in case the tank stirring is off (Figure 2.b).

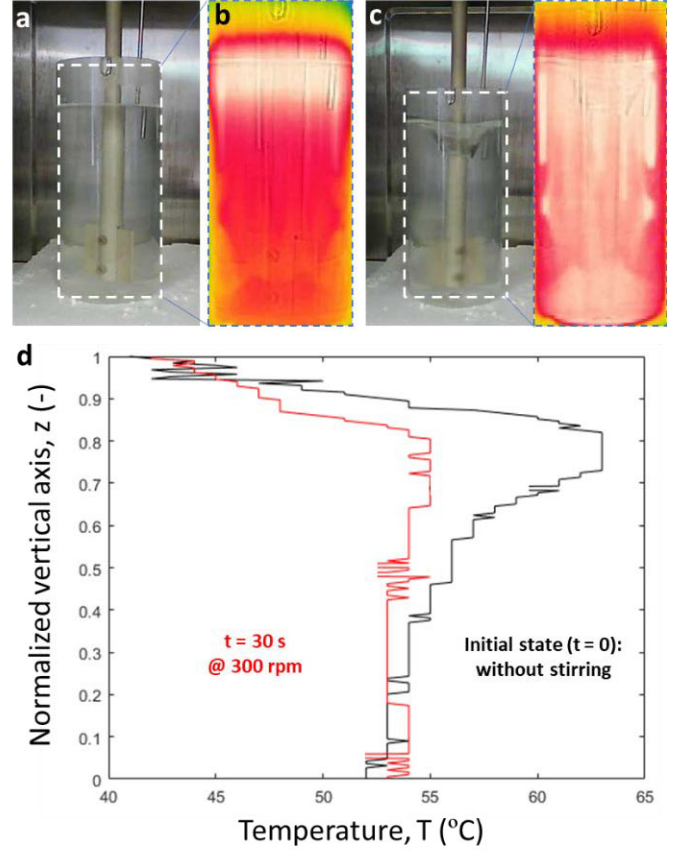


Fig. 2. a) Picture of the MW-heated vessel containing the polymer solution without stirring; b) thermal image of the heated vessel under without stirring; c) digital and thermal images of the MW-heated vessel after 30 s stirring at 300 rpm; d) quantification of the axial temperature gradient in the MW-heated vessel prior to (black) and after 300 rpm stirring (red). The normalized height of the free liquid surface is 0.8.

B. Electromagnetic field simulations

Regarding the minimum number of mode stirrer positions to be considered and averaged out for a reproducible sample heating pattern, it was found that the analysis of 8 positions (with an 45° angle offset) is enough. For a greater number of analyzed positions, the average EM field and, thus, the transient sample heating remain unchanged among simulation cases.

Figure 3.a shows the EM field distribution along the simulation domain, whereas 3.b shows a detail of such EM field at the boundary surface of the heated sample. According to this simulation result, the most intense EM field is located at the top open-end of the polymer solution as well as at the closest region of the lateral wall to the input ports.

C. Polymer solution heating

Figure 4.a shows the initial heating of the polymer solution sample after 1 second on stream. Despite the short heating time, it is already clear that the formation of hot spots at the sample domain exists, mainly due to the cavity configuration, relative position of the sample with respect to the input ports and sample

shape. The open-end of the sample and the region of the lateral walls that is closer to the input ports experience the fastest heating rate.

Figures 4.b and 4.c show the planar temperature projections in the parallel and normal axes with respect to the input ports alignment.

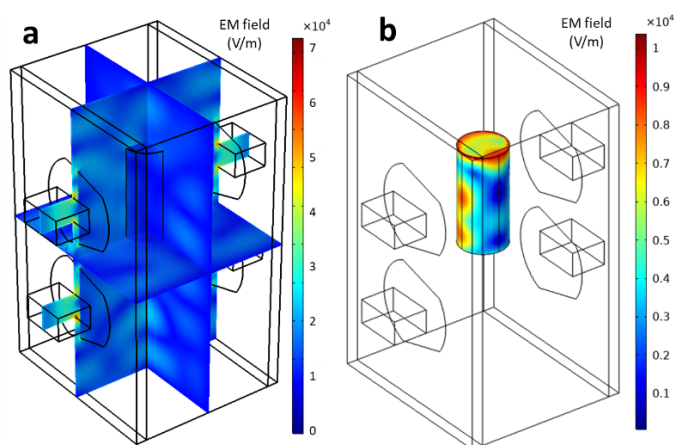


Fig. 3. EM field distribution averaged out from 8 field distributions obtained at 8 different mode stirrer positions (45° offset) along: a) the whole cavity domain, b) the sample domain

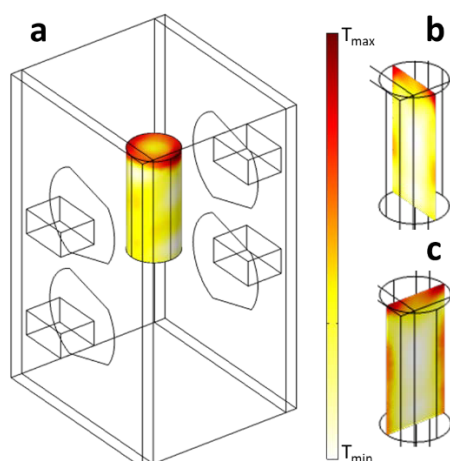


Fig. 4. a) Temperature distribution along the outer surface of the heated polymer solution after 1 second of MW irradiation (3 kW at 2.45 GHz); b) inner sample temperature profile in the transverse direction with respect to the wave propagation axis, c) inner sample temperature profile in the wave propagation direction.

Both projections suggest that the maximum sample temperature without tank stirring is found at the sample top open-end, as already observed experimentally (Figure 2.b). In addition, the locally overheated lateral regions aligned with the input ports found in the simulations were also observed experimentally (Figure 2.b and 2.c). This suggests that the assumptions made in the simulation model are appropriate.

V. CONCLUSIONS

The use of microwave-assisted heating for the chemical recycling of polymers is a very promising technology in line with the current trends of decarbonisation, process electrification and circular economy. The experimental and modelling approach tackled in this work showed that: 1) it was possible to attain the homogeneous heating of big polymer solution samples (up to 1 L) under MW irradiation by moderate tank stirring, being the temperature gradient $\Delta T < 2^\circ\text{C}$ for an average sample temperature of 55°C ; 2) it was possible to model and simulate this complex system using a commercial multiphysics software package and a discrete mode stirring turning speed approach. The model predictions in terms of temperature distribution are aligned with experimental findings.

ACKNOWLEDGMENT

This project has received funding from European Union's Horizon 2020 research and innovation program under the grant agreement No 820665-polynSPIRE project.

REFERENCES

- [1] A. Rahimi and J. M. García, "Chemical recycling of waste plastics for new materials production," *Nat. Rev. Chem.*, vol. 1, no. 6, p. 46, 2017.
- [2] A.L. Patricio-Silva, J.C. Prata, T.R. Walker, D. Campos, A.C. Duarte, A.M.V.M. Soares, D. Barcelón, T. Rocha-Santos, "Rethinking and optimizing plastic waste management under COVID-19 pandemic: Policy solutions based on redesign and reduction of single-use plastics and personal protective equipment", *Sci. Total. Environ.* Vol. 742, pp. 140565, 2020.
- [3] I. Vollmer, M.J.F. Jenks, M.C.P. Roelands, R.J. White, T.v. Harmelen, P. de Wild, G.P. van der Laan, F. Meirer, J.T.F. Keurentjes, B.M. Weckhuysen, "Beyond mechanical recycling: giving new life to plastic waste" *Angew. Chem. Int. Ed.*, vol. 59, pp. 15402–15423, 2020.
- [4] X.Tang, E.Y.X. Chen, "Toward infinitely recyclable plastics derived from renewable cyclic esters", *Chem*, vol. 5, pp. 284–312, 2019.
- [5] M. Solis, S. Silveira, "Technologies for chemical recycling of household plastics-A technical review and TRL assessment", *Waste Manag.* vol. 105, pp. 128–138, 2020.
- [6] U. Cesarek, D. Pahovnik, E. Zagar, "Chemical recycling of aliphatic polyamides by microwave-assisted hydrolysis for efficient monomer recovery", *ACS Sust. Chem. Eng.*, vol. 8, pp. 16274–16282, 2020.
- [7] Y. Fernandez-Diez, A. Arenillas, J.A. Menéndez, "Microwave heating applied to pyrolysis", *In. Tech.* vol. 72, pp. 723–752, 2011.
- [8] P. Priece, J.A. López-Sánchez, "Advantages and limitations of microwave reactors: from chemical synthesis to the catalytic valorization of biobased chemicals", *ACS Sust. Chem. Eng.* Vol.7, pp 3–21, 2019.
- [9] G. Stefanidis, A. Navarrete-Munoz, G.S.J. Sturm, A.I. Stankiewicz, "A helicopter view of microwave application to chemical processes: reactions, separations and equipment concepts", *Rev. Chem. Eng.*, vol. 30, pp. 233–259, 2014.
- [10] H. Kumiawan, S. Alapati, W.S. Che, "Effect of mode stirrers in a multimode microwave-heating applicator with the conveyor belt", *Int. J. Prec. Eng. Manufact. Green Technol.* Vol. 2, pp. 31–36, 2015.
- [11] W.C. Zhang, J.W. Tao, K.M. Huang, R. Perrussel, "An alternative method to model the mode stirrers in microwave cavity", 18th Int. Symp. Elec.Magn.Compat. 2016.
- [12] G. Brodie, "Energy transfer from electromagnetic fields to materials", *InTechOpen*, 2019.